TEXT-BOOKS OF CHEMICAL RESEARCH AND ENGINEERING

MOLECULAR PHYSICS

AND

THE ELECTRICAL THEORY OF MATTER

BY

JAMES ARNOLD CROWTHER,

M.A., SC.D., F.INST.P.

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PREFACE TO THE FOURTH EDITION

THE progress of Science is, nowadays, a generally accepted commonplace, but no one can be more acutely aware of how rapid this progress is than the author of a volume such as the present, who finds himself faced, from time to time, with the pleasant but by no means easy duty of attempting to keep his book abreast of the modern developments of his subject. In no part of physics has the advance been more rapid than in the investigation of the properties and structure of the atom. New experimental methods have enabled us to sound the depths of the atom and to map out its levels with the certainty of an oceanographical survey. Sir Ernest Rutherford and his students are already battering down the defences of its innermost citadel, the nucleus, with their atomic projectiles, while the work of Bohr and other quantum mechanicians is giving a theoretical basis for the experimental observations.

As these developments were foreshadowed in the previous edition they have involved an extension rather than a revision of the text. To make room for so much additional material without unduly increasing the size of the book I have been compelled reluctantly to abbreviate the accounts of the earlier theories of atomic structure; reluctantly, because the methods by which science advances are as interesting and as valuable as the results which it achieves. I have tried to preserve sufficient of the original material to illustrate the historical development of the subject.

It has been suggested by friendly critics that the title "Molecular Physics" is hardly a fair description of the contents of the book. I had hoped that "molecular"

would be read in its etymological rather than in its strictly technical sense, and be taken to cover all those tiny masses with which the book concerns itself. To meet the objection the book now appears with a new sub-title, which I hope will make all plain. In conclusion, I can only express my hope that this Fourth Edition will continue to fulfil the purpose of its predecessors by presenting a coherent and intelligible account of the present state of the electrical theory of matter.

J. A. C.

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MOLECULAR PHYSICS

CHAPTER I

INTRODUCTION

THE history of the rise of molecular theory has often been written. From Dalton, who first gave to the conceptions of the early atomists a definite meaning and a real experimental basis, through Avogadro and his fertile hypothesis of the molecule, and so on to the kinetic theory of Clausius and Maxwell, the story is told in almost every text-book of Chemistry and Physics, and is familiar as household words to all their readers. Here for a time science seemed to pause in her progress. It seemed as if the memoirs of these brilliant mathematicians were to contain the last word in molecular theory.

If this had been so, the following pages would have been superfluous. In recent years, however, new fields have been opened to the students of molecular phenomena; new methods of approach have been evolved so potent in character that subjects about which we had until then barely sufficient ground for speculation are now laid open to direct experimental attack. The molecule has been raised from a conception only realisable experimentally in millions to the rank of a definite particle whose entry into our apparatus produces a definite and measurable effect. At the same time the accuracy, and what is still more important, the certainty, of our measurements of molecular magnitudes have been enormously increased. It seemed, therefore, neither undesirable nor devoid of interest to attempt to re-write the subject of molecular physics, not from the standpoint of the kinetic theory, by which it was approached historically, and which

constituted for many years the sole line of attack, but rather in the light thrown upon these problems by the recent developments in what has come to be known as the "New Physics."

In order to fix our attention upon the problems to be dealt with, and to recall to our minds some clear ideas of the magnitudes with which we shall have to deal, it may be well to consider briefly the position to which we had been brought by the exponents of the kinetic theory.

The atom itself was a purely chemical conception. It took its rise in an attempt to explain the laws of chemical combination, and represents the smallest mass of an element which can take part in a chemical reaction. By its first exponents it was regarded as homogeneous and indivisible. This view is no longer held. We shall see later that we must conceive of the atom as something approaching a planetary system on an infinitesimal scale. A study of the phenomena of radioactivity has driven us to believe that in them we are dealing with a true decomposition of a true chemical atom; that the element radium is in fact a decomposition product of the atom of uranium, and is itself in the course of transition into an atom of lead, with the emission during the process of several atoms of helium.

In compounds the atoms of the different elements were supposed to be grouped together into similar particles or molecules, the ratio of the masses of the components being the same in each individual molecule as in the compound as a whole. It was soon found necessary to assume that even in the elements the atoms were usually connected into groups of two or more to form a larger particle, which, unless taking part in a chemical reaction, moved and acted as a single system. This extension of the theory was due to Avogadro, and his additional hypothesis that the number of these molecules in a given volume of gas under similar conditions is independent of the nature of the gas was the first great generalisation in the physics of the molecule.

It was soon realised that these molecules were particles exceedingly small in size. Various attempts to determine the approximate diameter of the molecules all led to the result that it was not very much greater than 2×10^{-8} cms. Various illustrations have been employed to assist us to grasp the extreme minuteness of this quantity. If, for example, a drop of water were to be magnified to the size of the earth the molecules in it would be of the size of footballs. Or again, as a recent writer has suggested, we may say that the carbon atom in the printed page subtends at the reader's eye the same angle as would be subtended there by a man on the moon.

The number of molecules in any visible portion of matter is, of course, correspondingly large. According to the latest determinations the number of molecules in 1 c.c. of air under normal conditions (0° C. and 760 mm. pressure) is $2{\cdot}7 \times 10^{19}$. It is almost hopeless to attempt to conceive this inconceivable swarm of particles. It may, perhaps, be of some assistance to point out that in the highest attainable vacua, when the pressure of the gas is not more than $\frac{1}{10000}$ mm. of mercury, the number of molecules present in every cubic millimetre of the space still exceeds 2,000,000,000.

In a solid body we must regard the molecules as relatively fixed. They are indeed in rapid vibration about their mean position, such vibration constituting the phenomenon which we know as heat. The fact that ancient gems and coins have come down to us through many ages still preserving their sharp outlines and their beautiful and clear-cut engraving shows that, in the absence of external forces, the defection of a molecule in a solid from its original station must be an exceedingly rare occurrence.

In liquids, however, we must regard the molecules as free to move. A liquid has no definite shape of its own, and two liquids if left quite undisturbed will gradually diffuse through each other with a velocity which is in general small but quite measurable. The different mole-

cules possess sufficient energy to escape from the attraction of neighbouring systems, but move only a very short distance through the thickly-crowded space before becoming entangled in other clusters.

Gases differ from liquids in the fact that the space occupied by a given number of molecules is very much greater; and a molecule, therefore, travels much further before coming into collision with other molecules. Thus a gramme of water substance when transformed into steam occupies 1,600 times the volume which it had in the liquid state. The molecules are therefore $\sqrt[3]{1,600}$ or, say, twelve times as far apart in the gas as in the liquid. The actual volume of the molecules themselves is thus only a very small fraction of the volume filled by the gas, the molecules occupying the space in which they are contained not by filling it with their bulk, but by moving about in it in all directions with considerable velocities. The tendency of a gas to spread through the whole of the space accessible to it thus represents the tendency of each molecule to proceed on its path in a straight line when not opposed by any obstacle, while the pressure on the boundaries of the gaseous space is due to the exceedingly rapid series of impacts made on them by the innumerable swarm of molecules in motion.

The velocity with which the molecules in a gas are moving can easily be calculated when the pressure and density are known. The mean velocity of a molecule of oxygen at the freezing point of water is about 425 metres per second, or about 1,000 miles per hour. It is, therefore, somewhat greater than the velocity of sound through air under the same conditions (331 metres per second). In addition to collisions upon the boundaries each molecule collides from time to time with other molecules of the gas, the number of collisions made by a single molecule under ordinary conditions of temperature and pressure being about 6,000,000,000 every second.

The distance travelled by the particle between two

collisions is known as its free path. Its actual value between any two collisions depends, of course, upon chance. Its mean value can, however, be calculated from the viscosity of the gas. For air under ordinary conditions it is about $7{\cdot}6 \times 10^{-6}$ cms., or roughly $\frac{3}{10000000}$ of an inch.

This mean free path, although a giant among molecular magnitudes, is still rather smaller than the smallest distance we may ever hope to perceive. Abbe has shown that two objects would have to be separated by rather more than twice this distance before they could be resolved by the best possible microscope working under the best conditions.

The mass of each molecule is, of course, exceedingly minute; according to the recent determinations of Millikan, which we shall describe later, the mass of a hydrogen atom is $1{\cdot}65 \times 10^{-24}$ gms., a number so minute that it can hardly be said to convey to the mind any impression at all. This number, it will be seen, represents the value in grammes of the chemical unit of atomic weight; the mass in grammes of any atom or molecule can thus be calculated from a table of atomic weights by merely multiplying the chemical atomic or molecular weight by this factor. Small as is this quantity, we shall see that its value is known with certainty to well within 1 per cent.

Of the quantities with which we have been dealing, the kinetic theory gave accurately the velocity of the molecule and the mean free path. It threw only a dim and somewhat uncertain light upon the number and mass of the individual molecules. As to the nature of the molecule, it can hardly be said to have given any information at all. It is at once the strength and the weakness of the statistical methods employed in the kinetic theory, that, given a sufficiently large number of molecules, their exact number, size, mass and properties become for many purposes matters of indifference. Thus many of the properties of gases were successfully deduced, in the first

place, on the assumption that the molecule was a hard sphere, an assumption which in the case, say, of a molecule like that of oxygen built of two atoms is almost certainly incorrect. It will be seen, then, how little light can be thrown upon the individual molecule by investigations of this nature.

As the molecule itself lay far beyond the limits of vision, and as the kinetic theory could afford so little certain information, it might have seemed that we must rest content with the knowledge already attained. Speculation as to the nature of the atom was not wanting, ranging from the simple hard atom of the original theory to the centre of force of Boscovitch, and the vortex atom of Sir J. J. Thomson, the early speculation of one who has done, perhaps, more than any other to render possible a true theory of the atom. These theories, ingenious as they were, withered for lack of experimental support, and the subject became gradually to be regarded as being in the realm of the unknowable. Meanwhile the great success of the statistical methods of the kinetic theory, the extension of thermo-dynamics, and the study of phenomena from a consideration of their equilibrium conditions, which followed on the work of Willard Gibbs, were leading further and further away from atomic and molecular hypotheses.

Fortunately one loophole remained into this region of the infinitely small. The kinetic energy of a particle is equal to the product of one-half its mass into the square of its velocity. However small the mass of the particle, therefore, we can theoretically by sufficiently increasing its velocity endow it with an appreciable amount of energy. In the case of a molecule the velocity required will, of course, be very large. The energy of a molecule in the air under normal conditions of temperature and pressure is about 5×10^{-14} ergs, assuming the mass and velocity already given. This is far too small to be detected. Let us suppose, however, that we can endow our molecule with a velocity much greater than this,

approaching 2×10^9 cms. per second. The energy of an oxygen molecule moving with such a speed would be $\frac{1}{2}(32 \times 1{\cdot}65 \times 10^{-24}) \, . \, (2 \times 10^9)^2$ ergs, or about 10^{-4} ergs. This, though small, is not less than can be appreciated in other forms of energy. Thus Lord Rayleigh has estimated that the faintest sound which can be heard transmits every second across a square centimetre of area at right angles to its path about $2{\cdot}3 \times 10^{-5}$ ergs. The energy in the faintest perceptible beam of light is not far different from this. Thus the energy of impact of a single molecule travelling with the velocity we have suggested would be comparable with the energy in a faint beam of light or a barely audible sound.

The velocity ascribed to the molecule in this calculation might seem impossibly large. It is in fact about $\frac{1}{15}$ of the velocity of light, and a particle travelling with this speed would, therefore, cover the distance from the earth to the sun in two hours. Such particles, however, actually exist, and it is the discovery of these particles and the measurements made upon them that have led to the great advances in molecular physics which we are about to describe. Particles having this velocity are shot out in large numbers from radioactive bodies. To anticipate a little, we may say that the α-particles from radium consist of atoms of helium shot out with a speed of this order of magnitude, and bearing a positive charge. Thus it is that a single α-particle is able to cause a flash of light when it strikes upon a screen covered with a suitable material.

The α-particles consist of helium atoms only. Velocities approaching that of the α-particles can be given to atoms and molecules of other substances by passing an electric discharge through them in the gaseous state at very low pressures. The phenomena of the discharge tube have indeed afforded the best means of investigating the properties of moving electrified particles, and we shall proceed to their consideration immediately.

In order to complete our survey, we will anticipate so

far as to say that the first experimental investigation of these phenomena led to results of a startling nature. Professor Sir J. J. Thomson, as the result of a brilliant series of researches and deductions, which may truly be said to mark a fresh era in the progress of science, showed that the most conspicuous set of particles in the discharge tube, namely, those constituting the cathode rays, had a mass not more than $\frac{1}{1800}$ part of that of a hydrogen atom.

It was found, moreover, that whatever the nature of the gas through which the discharge was passing, whatever the nature of the electrodes used, the mass of the cathode particle produced and the magnitude of the charge carried by it were always the same. These cathode particles, corpuscles or electrons, as they came to be called, must thus be regarded as forming an integral part of the atom of every kind of substance. They are, therefore, even more fundamental than the atom itself, since they form part of the material from which the atom is built up. The methods used in their investigation are similar in principle to those which have recently been applied to atoms and molecules, but the special properties of the electrons rendered their experimental investigation less difficult than that of the atom or molecule, so that for a time it could truly be said that far more was known of the electron than of the atom itself. For these reasons we will commence our study of molecular physics with the consideration of the electron.

CHAPTER II

THE PHYSICS OF THE ELECTRON

The general appearance of an ordinary discharge tube is perhaps familiar to most of my readers. It is represented somewhat diagrammatically in Fig. 1. Covering the cathode C is a velvety light known as the cathode glow. Beyond this is a comparatively dark space, named after its discoverer, Sir William Crookes. If the pressure in the tube is fairly high this Crookes dark space will be so close to the cathode and so small as to be hardly visible.

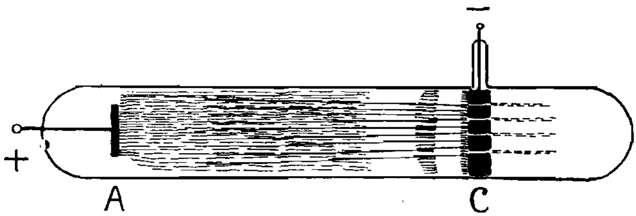

Fig. 1.—The discharge tube.

Beyond this dark space is another luminous area, the negative glow, bounded on the side remote from the cathode by still another obscure area, the Faraday dark space. The length of the tube occupied by these phenomena depends mainly on the pressure of the gas, and is practically independent of the length of the tube, the remainder of which, however long, is filled with a bright light known as the positive column, which is frequently, though not necessarily, divided into numerous striæ. It is the light from this positive column that is generally employed in the spectroscopic examination of gases in the discharge tube.

If the pressure is fairly low another phenomenon may

be distinguished. Proceeding normally from the cathode and moving in straight lines across the Crookes dark space may be seen faint bluish streams of light, known as the cathode rays. As the pressure is still further reduced these rays become relatively more and more important, and penetrate further and further, until finally they fall upon the glass walls of the discharge tube, exciting there a greenish phosphorescence. Meanwhile the Crookes dark space has grown until it occupies practically the whole of the tube, the remaining parts of the ordinary discharge being represented by the glow on the cathode and a single patch of light near the anode itself.

The nature of the cathode rays remained for some time in doubt. However, in 1895, Perrin showed that they carried a negative charge, and in the following year Professor Sir J. J. Thomson proved conclusively that they consisted of streams of negatively charged particles, moving with extremely high velocities, and having a mass in all probability much less than that of a hydrogen atom.

Let us continue for a moment the study of the discharge tube. It had long been known that if a solid obstacle were placed in the path of the discharge a shadow of the object was cast by the cathode rays on the opposite wall of the tube. It was noticed that if the obstacle was placed within the Crookes dark space a shadow was also cast on the cathode. That is to say, there must also be rays in the tube proceeding in the opposite direction to the cathode rays and falling upon the cathode itself. By using a perforated cathode, as shown in the diagram, these rays become visible as faintly luminous streaks of light, coming through each of the perforations, and exciting a faint mauve phosphoresence where they strike the walls of the tube. These rays, which carry a positive charge and have a mass comparable with that of an atom, are formed by the positive particles to which we have already alluded.

The high velocities of these particles give them, as we have seen, sufficient energy to produce luminous effects when they fall upon suitable screens. The additional fact

that they carry an electric charge enables us to determine not only the velocity, but also the ratio of the mass of the particles to the charge which they carry.

The general problem of the motion of an electrified particle when moving under the action of electric and magnetic forces is one of some little complexity, though complete solutions have been given by various mathematicians. Fortunately the special cases which are required for our present purpose lend themselves readily to the simplest treatment.

Suppose that a particle of mass m and charge e is moving with a velocity v at right angles to a magnetic field of strength H. In one second the charge e will have moved through a distance v cms. We may therefore regard the path of the particle as a sort of conductor v cms. long, carrying an electric current whose strength is e. The mechanical force on such a conductor when placed in a magnetic field is known from the laws of electro-magnetism to be equal to the strength of the field multiplied by the current and the length of the conductor, that is to the product $H . e . v$. Further, this force is at right angles to the direction of the current and to the lines of force in the magnetic field. A little consideration will show that under these circumstances the path of the particle is changed from a straight line to a circle described in a plane at right angles to the direction of the lines of force in the magnetic field.

Let r be the radius of this circle. A particle of mass m moving round a circle with a velocity v exerts a centrifugal force, tending to urge it away from the centre of the circle, equal to

$$m . v^2/r.$$

Now for equilibrium the force tending to urge the particle away from the centre must equal the force due to the magnetic field tending to draw it in. Thus we have

$$H . e . v = m . v^2/r$$

$$\frac{m}{e} . v = H . r \quad . \quad . \quad (1)$$

Again the particle carries an electric charge. It can therefore be deflected by an electric field. Let X be the strength of the electric field. Then the force experienced by the particle is equal to X . e and acts upon the particle in the direction of the lines of electric force. If now we arrange our apparatus so that the electric field and the magnetic field are at right angles to each other, the forces upon the particle due to the two fields will act along the same straight line, and by properly adjusting the sign of the electric field we can make the two forces oppose each other. It will then be possible to find a value for the electric field such that the two forces just neutralise each other and the particle goes on its path without deflection. In this case we must have

$$\mathrm{H} \cdot e \cdot v = \mathrm{X} \cdot e$$
$$v = \mathrm{X}/\mathrm{H} \quad . \quad . \quad . \quad (2)$$

Thus if we apply to the moving electrified particle simultaneously an electric and magnetic field of such magnitudes that the particle pursues its path without any deviation, the ratio of the strengths of the two fields will give us directly the velocity of the particle. If, further, we can measure the radius of the circle into which the path of our article is bent by the action of the magnetic field alone, we can, by equation (1), determine the value of the ratio m/e, or the mass to the charge for the particle we are investigating, since the value of v is now known from the previous experiment.

This ratio of the mass to the charge is one of the utmost importance in molecular physics. It may be noted that for ions in solution it is the quantity of matter associated with the transference of unit quantity of electricity, that is to say, the electro-chemical equivalent. According to the latest values, the electro-chemical equivalent of hydrogen ions in solution is ·0000104 gm. per coulomb. The values of the ratio for other ions can be deduced from this and a table of combining weights in the usual way, since every ion in solution carries by Faraday's laws either

the same charge as the hydrogen ion or some simple multiple of it.

Owing to the way in which the volt and the ohm have been defined, the former as 10^8 and the latter as 10^9 absolute electro-magnetic units, the absolute unit of electro-magnetic charge is ten times the coulomb or practical unit of charge. The value of m/e for hydrogen

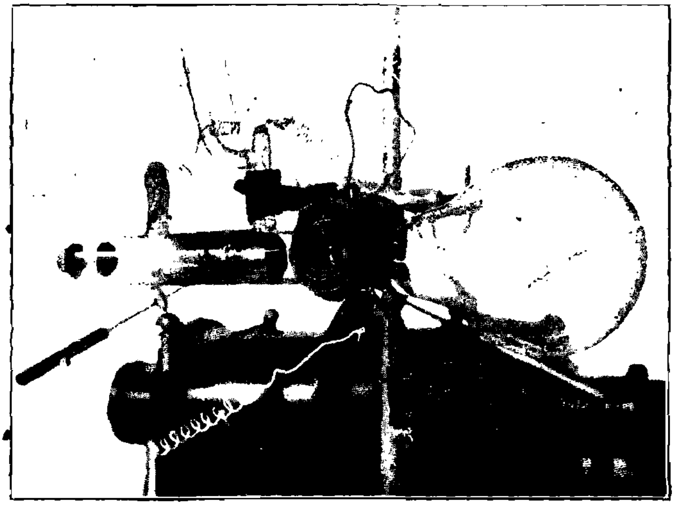

FIG. 2.—Cathode ray deflection tube.

in absolute units of charge is, therefore, ·000104, or just a little greater than 10^{-4} gms. per absolute electro-magnetic unit of charge.*

The principles just explained found their first application

* The science of electricity is burdened with two distinct systems of units for the measurement of electrical magnitudes, the one founded on the consideration of the force with which two similar charges repel each other, the other on considerations of the induction of currents by magnets. The practical system of units is founded upon the latter, the volt being 10^8 and the ohm 10^9 absolute electro-magnetic units. The ampere and coulomb are thus one-tenth of the absolute units of currents and charge.

in the experiments of Professor Sir J. J. Thomson on the cathode rays, experiments which may well be said to mark a new era in science. The experimental methods used by him have been modified and improved upon in the light of subsequent discoveries, and the accuracy attained in the measurements greatly increased. In principle, however, the experiments remain the same, and on account of its historic interest the original apparatus used in these experiments will be described. Fig. 2 is taken (by kind permission of Professor Sir J. J. Thomson) from a photograph of one of the tubes used by him for the experiment. The arrangement of the various parts will

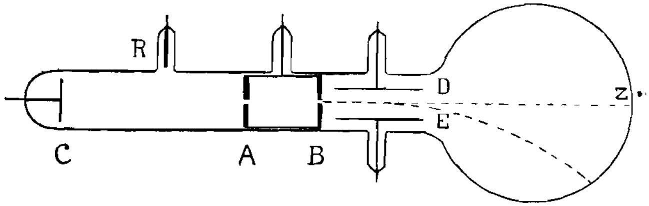

FIG. 2A.—Diagram of cathode ray tube.

be seen more clearly from the diagrammatic representation in Fig. 2A.

The cathode of the discharge tube is at C, and consists of an aluminium disc supported by a rod of the same metal and connected with the outside of the tube by a platinum wire sealed through the glass. The anode R is an aluminium rod placed in a side tube, while facing the cathode is a thick metal disc A, filling the tube but pierced with a

To make confusion worse confounded, it has become usual in books and original papers on these subjects to give the value of m/e in electro-magnetic units, while the value of e itself is usually given in electrostatic units. Our statement that the force on the electron due to the magnetic field is equal to H . e . v implies that we are using the absolute electro-magnetic system of units, as this system has been defined in such a way as to make this statement true. As this system is the one more closely related to the units in practical use, we shall employ it throughout, except where the contrary is explicitly stated.

small hole through which the cathode rays can pass in a narrow pencil. To define this beam of rays still further, a second metal disc B pierced with a still finer hole is placed some distance behind A. For convenience these two discs are mounted in a metal tube, as shown in the figure. This tube and the anode R are connected to earth, while R and C are connected to the terminals of a large induction coil, as shown in the photograph.

Thus, when the discharge is passed between C and R, a very fine well-marked pencil of cathode rays emerges from B. It is then made to pass between two parallel plates D and E of aluminium which can be charged to any required difference of potential by connecting them to a large battery of small accumulators.

This part of the tube is also placed between the poles of the little electro-magnet shown in the photograph, the lines of magnetic force being at right angles to the plane of the paper, and therefore at right angles to the electric field. Finally, the stream of cathode particles falls upon the walls of the bulb Z, which are covered with powdered zinc-blende, its presence being marked by a spot of bright green phosphorescent light at the point of impact. The position of the spot in the original experiments was read off on a paper scale pasted on the outside of the tube.

To perform the experiment the magnetic field is first applied and the deflection of the spot of light measured. From this deflection and the dimensions of the different parts of the tube it is possible to calculate the radius of the circle into which the path of the rays has been bent by the magnetic field. The deflected and undeflected paths of the particles are indicated by the dotted lines in the diagram. The electric field is then applied and the difference of potential between the two plates gradually increased until the spot of light is brought back to its original position. The ratio of the electric to the magnetic field is then equal to the velocity of the cathode particles. The value of the ratio m/e can be calculated from this

velocity and the known magnetic deflection as explained above.

The experiments were not without difficulty. It was at first very difficult to obtain any deflection of the particles by means of an electric field. This was found to be due to the fact that the passage of the cathode rays through the residual gas in the discharge tube rendered it more or less conducting, so that the particles were moving through what was practically a closed conductor, and were thus hardly affected by the external electric field. It was necessary in order to eliminate this effect to work with very high vacua.

On making the calculations it was found that the velocity of the particles depended principally upon the potential of the discharge, and to some extent also on the pressure of the residual gas in the tube and the nature of the electrodes and the gas in the tube. Even in the same tube the velocity of all the rays was not the same, so that on applying the magnetic field the single spot of light made by the cathode beam on the zinc-blende screen was spread out into a little magnetic spectrum, as we may call it, each point of which corresponded to cathode rays moving with some definite velocity. In tubes at an exhaustion suitable for these experiments the velocities range, as a rule, from 2×10^9 to 3×10^9 cms. per second, or about one-tenth of the velocity of light.

On evaluating the ratio m/e it was not found to suffer similar variations. The original experiments showed—and this has been confirmed by many subsequent experiments—that, whatever the nature of the gas in the discharge tube, whatever the material of the cathode, whatever the working potential of the tube, the value of the ratio of the mass of the cathode particle to its charge is always the same. According to the latest determinations, the value of this constant is $5{\cdot}67 \times 10^{-8}$ gms. per unit of charge.

Again, although we have so far considered only the case of the cathode rays, they are not by any means the only

source of these corpuscles, or *electrons* as they are now called. Similar electrons are given off in quantities from a clean metal surface when illuminated by ultra-violet light, or from the surface of the liquid sodium-potassium alloy under the action of the light from an ordinary

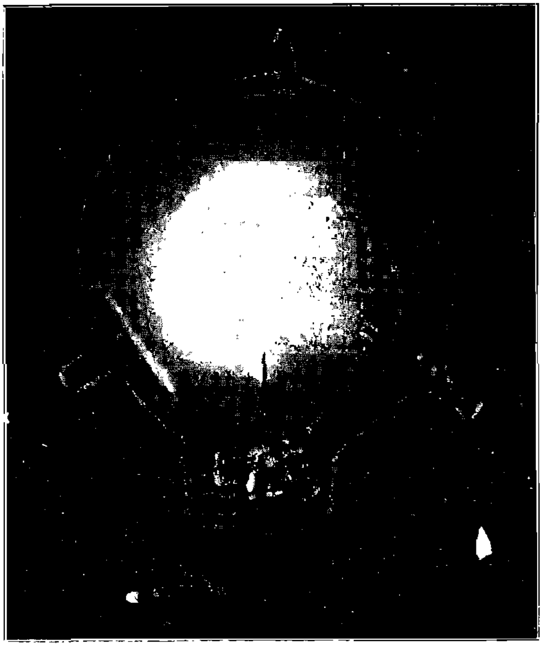

FIG. 3.—Magnetic deflection of the cathode rays.

candle. X-rays produce them whenever they fall upon any material object, and it is interesting to note that the velocity of the electrons thus produced is the same as that of the cathode rays in the Crookes tube from which the X-rays proceed. Electrons are also emitted from incandescent metals at a high temperature, and in very large quantities when certain metallic oxides, notably

those of barium and calcium, are raised to a red heat. This method of producing electron emission is now employed extensively in the "wireless" valve and the Coolidge X-ray tube. These electrons have very little velocity of their own, but may very readily be given one by acting upon them with an electric field. If the heated oxide is raised to a potential P in absolute units, the work done on the electron by the field will be P . e. If v is the velocity acquired by the electron, its kinetic energy is $\frac{1}{2}mv^2$. Hence, by the principle of the conservation of energy $P . e = \frac{1}{2}mv^2$ or $v^2 = 2P . e/m$. Thus by suitably altering the potential of the hot oxide we can give to these electrons a suitable and known velocity.

Fig. 3 is a reproduction of an actual photograph of such a discharge. The cathode is a platinum strip carrying a minute speck of barium oxide, raised to a red heat by means of an electric current and charged to a potential of − 240 volts from a cabinet of small accumulators. The electrons given out by the heated BaO are projected by the field in a narrow pencil and are rendered visible by their action on the residual molecules of air in the exhausted tube. In the photograph a magnet has been placed behind the tube so that there is a magnetic field at right angles to the paths of the electrons, which are thus bent into the arc of a circle as shown in the figure. The fact that the circle is not completed is due to the gradual diffusion and absorption of the electrons by collision with the molecules of the gas in the tube.

The value of the ratio m/e for these electrons has been measured by their discoverer, Wehnelt, and others. It may be noticed that as the potential P to which the cathode is raised is equal to $\frac{1}{2}v^2 . m/e$, it is only necessary to measure the radius of the circle into which the rays are bent by a magnetic field of known strength H in order to be able to calculate both v and m/e. This fact has been applied by Lenard and others to measure the value of m/e for the electrons given off by metallic surfaces under the action of ultra-violet light.

TABLE I

Observer.	Source of Electrons.	e/m e.m.u. per gm.
Kaufmann .	Cathode rays . . .	$1{\cdot}77 \times 10^7$
Simon .	.. ..	$1{\cdot}72 \times 10^7$
Classen .	.. ..	$1{\cdot}774 \times 10^7$
,, .	Hot lime	$1{\cdot}776 \times 10^7$
Woltz .	β-rays (slow) from radium .	$1{\cdot}767 \times 10^7$
Bucherer .	,, ,, ,, .	$1{\cdot}763 \times 10^7$
Bestelmeyer	Hot lime	$1{\cdot}766 \times 10^7$

The above table (Table I.) gives a few of the more recent determinations of the ratio e/m for electrons from different sources. It will be seen that within very narrow limits indeed, especially considering the difficulties of the experiments, the ratio of the charge to the mass is the same for all electrons, whatever their origin and whatever their velocity, and differs very little from $1{\cdot}77 \times 10^7$. The value of m/e or the electro-chemical equivalent of the electron, if we may so call it, is therefore $5{\cdot}67 \times 10^{-8}$. For the hydrogen atom, as we have seen, the value is about 10^{-4}. If we assume that the charge e on an electron is the same as that on a monovalent ion in solution we see at once that the mass of the electron must be only $\frac{1}{1845}$ part of that of the hydrogen atom.

For this assumption, however, very little direct evidence could be adduced at the time when it was first made by Sir J. J. Thomson. It was one of those strokes of genius which have proved to be correct. To determine absolutely the mass of an electron we must find some method of determining the value of the electronic charge e. Fortunately this also has proved possible, owing to a discovery made in the Cavendish laboratory by Mr. C. T. R. Wilson.

If a space saturated with water vapour is suddenly chilled the surplus water over and above that which would saturate the space at the lower temperature in general separates out as little drops, forming within the space a

thick mist or cloud. It was, however, shown many years ago by Aitken that this condensation always commences round minute particles of dust, particles often far too small to be visible, yet sufficiently material to be caught by a well-packed tube of cotton wool. In the absence of these particles he found that a very considerable degree of supersaturation could be produced without any deposition of water and without any appearance of cloud or mist, and that it was only when the supersaturation became at least eightfold that a mist or cloud was produced. It appeared then that for a lesser degree of supersaturation than this the water vapour must have some nucleus about which to condense before a drop could be formed.

Gases under ordinary conditions are almost perfect insulators. Under the action of certain agents, such, for example, as X-rays or any of the rays from radioactive substances, a gas becomes more or less conducting. It has been shown that this is due to the creation in the gas of systems, some negatively, some positively charged. In all probability these are produced by the ionising agent expelling a negative electron from the atom through which it passes, leaving the remainder of the molecule positively charged. The negative electron thus set free soon attracts to itself an uncharged molecule of gas, just as an uncharged pith ball is attracted by an electrified ebonite rod. The gas thus becomes filled with positively and negatively charged molecules, which move under the action of an electric field in exactly the same way as the ions of an electrolyte in the electrolysis of a solution. There is this difference, however, that, whereas the electrolytic ions are stable, the gaseous ions, if left to themselves, gradually recombine to form neutral molecules. Thus unless the supply is kept up by the continuous action of the ionising agent the conductivity soon dies away.

The mechanism of ionisation by the electrons emitted by a metal plate under the action of ultra-violet light is somewhat different. Here the electrons given off have not sufficient energy to expel an electron from the atoms

of the surrounding gas and thus no positive ions are produced in the gas. The negative electrons, however, attract to themselves neutral molecules and form negative ions. It is evident from the mode of formation that these ions bear the same charge as the electron which gave rise to them, that is to say, their ionic charge is the same as the electronic charge e. It may be pointed out in passing that since the ions are all of the same sign and produced at the same place, namely, the surface of the metal plate, a current can only be sent through the gas in one direction. If the metal plate is negative the ions will be repelled and thus carry a negative current from it to the positive electrode. If, however, the plate is positively charged the ions will be attracted back to it by the field and the gas will remain an insulator.

It occurred to C. T. R. Wilson that these ions might possibly serve as nuclei for the production of a fog or cloud in supersaturated air, and this was found on experiment to be the case. He was able to show that drops of water would condense on these negative ions when the supersaturation was only fourfold, while condensation occurred on positive ions also when the supersaturation was sixfold. It was found that when the supersaturation was raised to the proper degree each negative ion became the centre of a single drop of water, and if the conditions were fairly uniform these drops were all of the same size. It will be remembered that in the case of the ions formed by ultra-violet light each of these drops will carry with it the electronic charge e, the magnitude of which we wish to determine.

Every drop in a cloud is falling through the air under the action of gravity with a definite velocity. Clouds do not float in the air, though if the drops are sufficiently small they fall very slowly, owing to the great surface they present, in comparison with their mass, to the viscous drag of the air. Sir G. G. Stokes has shown that if r is the radius of a small drop of water and q the viscosity of the air, the velocity with which the drop will fall relative to

the air is $\frac{2gr^2}{9q}$, where g is, as usual, the acceleration due t gravity. The drops formed round the ions are all of th same size and fall at the same rate. We can thus measure the velocity v of their fall by watching the rate at which

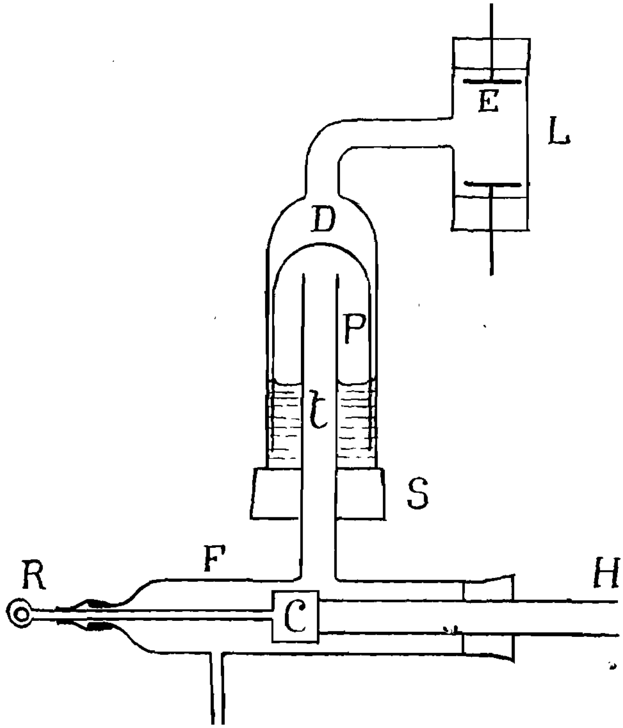

Fig. 4.—C. T. R. Wilson's expansion apparatus.

the surface of the cloud settles. This will enable us to calculate the radius r of the drop, and hence its mass M.

So far the cloud has been falling freely under the action of gravity. Let us apply a field of strength X in such a direction as to oppose the action of gravity, that is to say, with the positive plate above the cloud. The

force on each drop due to the electric field is then X . *e*, while that due to gravity is M . *g*. We can adjust the field X until these two forces exactly balance each other, and the drop remains suspended in air like Mahomet's coffin. When this stage is reached we have

$$X \cdot e = M \cdot g$$

or

$$e = M \cdot g/X \quad . \quad . \quad . \quad (3)$$

But all these quantities are known, and thus the charge on that drop of water, which we have shown to be the same as that on the original electron, can be determined.

It remains to describe the apparatus devised for the experiment. It is shown in Fig. 4. It is well known that if a mass of gas is expanded in such a way that no heat is allowed to enter or leave it, the temperature will fall. The lowest temperature reached in any given expansion can be calculated from the gas laws if the ratio of the specific heats of the gas is known. As gases are bad conductors of heat we can satisfy the conditions of the experiment by making the expansion sufficiently rapid. The mass of the gas is then cooled down to the calculated temperature before any appreciable amount of heat has had time to enter the system.

The method of making the expansion will be clear from the diagram. The tube H connects with a large vessel of some litres' capacity kept exhausted by means of a water pump. It is closed by a rubber stopper C, which can be suddenly withdrawn by means of the rod R, thus creating practically instantaneously a partial vacuum in this part of the apparatus. The air being thus suddenly withdrawn from beneath it, the light glass plunger P, which had been adjusted to a suitable height in the cylinder D, is forced down with great rapidity, thus producing within the experimental chamber L a very rapid expansion of an amount which depends only upon the initial position of the plunger P. The temperature in L is therefore suddenly lowered to a degree which can be calculated, and if the air in L was previously saturated, it will now be super-

saturated to an extent which is measured by P/*p*, where P and *p* are the vapour pressures of water at the initial and final temperatures.

In making an experiment the air in L is freed from all material nuclei by repeated expansions ; the plunger is adjusted so as to make the supersaturation after expansion rather more than fourfold, the upper plate E, which is usually of zinc, is illuminated with ultra-violet light for a moment in order to produce a suitable supply of negative ions in the gas and the expansion is made. A cloud is formed on the negative ions and the rate at which the surface of it settles is taken. After it has fallen some little distance the upper plate E, which had been previously uncharged, is raised to a positive potential and its potential adjusted until the surface of the cloud is seen to remain stationary. If V is this potential and the lower plate at a distance *d* from the upper one is earthed, the strength of the electric field is V/*d* and the electronic charge *e* is equal to M*gd*/V, where M has been calculated by Stokes' law from the rate of fall of the cloud.

The method was first applied in a rather different form by Professor Sir J. J. Thomson. In the form described, which is the one which has been used with the greatest success, it was performed by H. A. Wilson. We have, for the sake of making our argument logically complete, considered the case of the electrons produced by ultra-violet light, for in this case we have direct evidence that the charge we are measuring is really that carried by an electron. It has been shown, however, experimentally that the value of the charge *e* is the same no matter how the ions are produced. Experiments carried out with ions produced by X-rays or the various rays from radioactive materials give exactly the same values for the charge *e*. Like the ratio *m*/*e*, the charge *e* is a universal constant. Some recent determinations of it are given in the table on page 25.

It will be seen from Table II. that the values obtained for the electronic charge *e* by different observers working

TABLE II

Observer.	Carrier.	e (electrostatic units).
Begeman .	Water drops (original method)	$4{\cdot}67 \times 10^{-10}$
Roux .	Sulphur drops . . .	$4{\cdot}17 \times 10^{-10}$
Ehrenheft .	Metallic dust . . .	$4{\cdot}65 \times 10^{-10}$
Millikan .	Oil or mercury spray . .	$4{\cdot}774 \times 10^{-10}$
Rutherford	Counting the α-rays . .	$4{\cdot}65 \times 10^{-10}$
Planck .	Theory of radiation . .	$4{\cdot}69 \times 10^{-10}$

in different ways, though not so consistent as those obtained for the ratio e/m, yet do not differ much from a mean value of about $4{\cdot}77 \times 10^{-10}$ electrostatic units, or $1{\cdot}59 \times 10^{-20}$ in the absolute electro-magnetic unit of charge which is equal to 10 coulombs.

The most extensive survey of the subject has been made by Millikan. Instead of water drops he used very fine globules of oil or sometimes of mercury produced by an atomiser or fine spray. These drops could be passed as required into his apparatus, which very much resembled the chamber L in Fig. 4, through a small hole made in the top plate. These globules did not evaporate appreciably, so that an individual drop could be isolated and kept under observation through a microscope for several hours consecutively. The microscope was fitted with an engraved glass scale in the eyepiece, on which the whole of the measurements on the motion of the drop could be made very accurately and conveniently. By properly adjusting the difference of potential between the upper and lower plates the drop could be kept in the field of view during the whole of the experiment. The measurements made and the calculation of the charge are precisely the same for the oil globule as for the water drop.

The globules were not originally charged, but picked

up their charges from the surrounding air, which was ionised either by X-rays or by radium. These comparatively large globules could collect and carry more than one electronic charge, seven or eight being a very usual number, though some drops had many more than this. The interchange of charges between the globule and the air could be easily observed with the microscope. The drop which had been poised almost motionless in the air for some time by the balanced action of gravity and the electric field would be seen to dart suddenly upwards, showing that the drop had captured another charge and thus caused the electric force to increase, or perhaps on the other hand the drop would be seen to fall, having parted with one of its charges to some colliding molecule.

The important point brought out by the experiment is that in every case it was found that the magnitude of the charge thus exchanged, which could be calculated by a simple application of the principles already explained, was exactly the electronic charge e, and the total charge on the globule at any time was always very exactly some integral multiple of this charge. An examination of the mass of figures collected by Professor Millikan leaves no room for doubting that the charge which we have denoted by e is a universal constant, and that every electrical charge is made up of an integral number of electrons, just as every fragment of an element is made up of a whole number of atoms.

From Table I. we have the ratio e/m, equal to $1{\cdot}77 \times 10^7$, for all electrons. Combining this result with the value just obtained for e, we are driven to the conclusion that whatever the source from which they come all electrons have identically the same mass and charge, the former being 9×10^{-28} gms., the latter $1{\cdot}59 \times 10^{-19}$ coulombs. Such particles must form a constituent part of all matter.

The value of e ascribed to Professor Rutherford and also included in Table II. was obtained from experiments of an entirely different nature made on the α-particles. Before passing to these we must refer very briefly to an

exceedingly beautiful extension of the methods of drops which has recently been brought to perfection by the originator of the experiments.

In the experiments already described, the clouds

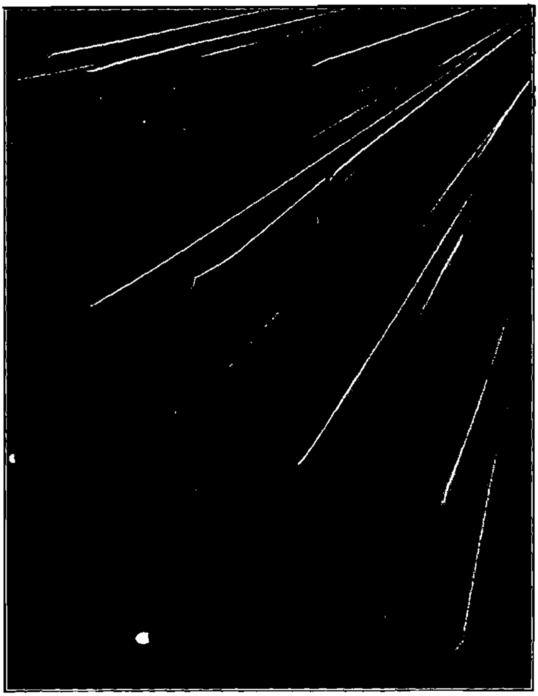

Fig. 5.—The tracks of the α-particles.

obtained were fairly uniform, as the ionisation was intense and time was given for the ions formed to diffuse through the body of the gas. Suppose, however, that we allow, say, a single α-particle to cross our expansion chamber and at the same time make an expansion of the air in the chamber by the method already described. The particle passes through the air, ionising it as it passes,

and thus leaving behind it a trail of charged ions. Water drops at once form upon these from the now supersaturated air before they have had time either to diffuse into the rest of the gas or to recombine. If the expansion chamber is suitably illuminated these drops appear as brilliant points of light all along the path traversed by the particle. In the case of the α-particle the ions are so numerous that the track of the particle appears as a continuous shining streak of light. In the case of an electron where the ionisation is less intense the appearance presented is that of a string of bright beads. We are thus able not merely to detect, but even to follow the path of a single particle of any kind providing it produces ionisation in a gas.

FIG. 6.—X-rays.

By the kindness of Professor C. T. R. Wilson, I am able to reproduce two of the photographs taken by him in this way. In Fig. 5 are shown the paths of a number of α-particles. These have their origin in a small sample of radium placed just outside the chamber and shoot across the chamber as shown in the photograph until finally their energy, which is being spent in the work of separating the ionic charges along the whole of the path, becomes too small to produce ionisation, and the particles disappear from human ken.

Fig. 6 is a photograph of the passage of a narrow beam of X-rays through the expansion chamber, from A to A′. We have mentioned before that X-rays produce rapidly-moving cathode rays when they fall upon matter ; in this remarkable photograph these cathode rays are made visible to us by the ions they produce. Here upon the dark background their tracks may be seen as a tangled skein of bright threads radiating out from the invisible track of the X-rays. Each single thread represents the whole path of a single electron from its expulsion from the parent molecule under the action of the X-rays, to the place where it finally becomes too weak to ionise. In some of the brighter threads the individual drops are clearly to be seen. The twists and turns in each little path are due to collisions between the cathode particle and the molecules of the surrounding air.

These photographs will perhaps do more than any argument, however cogent, to remove any doubt which may still be felt as to the objective reality of the electrons and other particles with which we have been dealing. Nothing but an actual particle could leave behind it such tracks as those shown in the photographs we have reproduced.

We have not space to deal with the many difficulties of the experiment or with the skill and ingenuity with which they have been overcome. Those interested may be referred to the original papers in the *Proceedings of the Royal Society* from 1912 to 1924. This ingenious and powerful experimental method has now been applied with great success to many problems connected with the behaviour of ionising radiations, and apparatus of this kind is in constant use in many of the great laboratories of the world.

CHAPTER III

THE POSITIVE PARTICLE

We have already seen that positively charged particles are projected with high velocities from radium and other radioactive substances, and that they are also to be found in discharge tubes. Unlike the electron, the positive particle has a mass comparable with that of an atom, no positive charge having yet been detected in association with any mass less than that of a hydrogen atom. The charge on a positive particle is, however, either the same as that on an electron or some simple multiple of it. The α-rays, as the particles from radioactive substances are still called (a relic of the time when their nature was unknown), always carry a charge of $2e$. In discharge tubes, however, positive particles are found with all integral multiples up to $8e$. We shall see that we may regard the positive particles as atoms travelling with a high speed from which one or more electrons have been removed.

The positive particle can be deflected by electric and magnetic fields in the same way as the negative electron, and obeys the same laws. The deflection is in each case in the opposite direction to that of the electron, and, owing to the greater mass of the particles, much smaller. The great ionising power of the positive particles makes the detection of the electrical deflection difficult. These difficulties have now been overcome, and the positive particle also has been made to yield up some of its secrets. As the positive particle is always an atom of some kind, its investigation is, perhaps, from some points of view, of even greater interest than that of the electron.

The greater energy of these particles is, however, in

some ways an advantage. It enables us to deal with individual particles, whereas in the case of the electron we can only deal with large numbers. Thus our measurements gain, perhaps, in definiteness although they may lose somewhat in numerical precision.

If e be the charge on a single α-particle, the total charge carried by N particles is N . e, and if N is sufficiently large this charge will be large enough to be directly measured

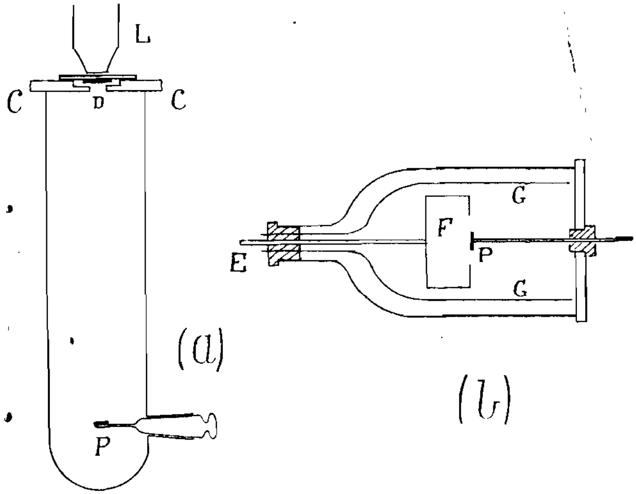

FIG. 7.—Regener's apparatus.

by an electroscope or electrometer. If we can further determine the number of the particles which conveyed this charge we shall have made a direct determination of the charge e.

The experiments are best performed using the α-particles from radium, polonium, or some other radioactive substance. They were carried out almost simultaneously by Rutherford and by Regener. In Rutherford's experiments the α-particle was detected by the ionisation it produced in a special chamber, the entry of each α-particle

into the apparatus being notified by a kick of the needle of a sensitive electrometer. In Regener's experiments the number of scintillations produced by the particles in a given time on a fluorescent screen was counted. The former method was the more satisfactory from a theoretical view, as there was at the time no direct evidence that every particle produced a scintillation when it struck a screen, although this has since been shown to be the case by Rutherford. It was also proved by the fact that the two experimenters reached almost the same value for the charge on the α-particle. The experiment of Regener is simpler to carry out than the electrical method of Rutherford, and granting his assumptions, is probably capable of greater accuracy.

Regener's apparatus is shown in Fig. 7. Fig. 7, *a*, shows the "counting" apparatus, Fig. 7, *b*, the apparatus for measuring the total charge carried by the rays.

The counting apparatus is very simple. It consists of a long tube closed at one end by a brass plate, *c*, *c*, bored with a circular hole some centimetre in diameter. Across this is sealed a thin glass coverslip bearing on its under surface the fluorescent screen D, in this case a thin plate cut from a crystal of brown diamond, a substance chosen by Regener after many trials as the most suitable for the purpose. Rutherford has since used prepared screens of powdered zinc-blende with equal success.

A high-power microscope was focussed on the diamond plate for viewing the scintillations, which, numbering about one every two seconds, were easily counted. The source of the α-particles in Regener's experiments was a plate of polonium, placed at P, some 12·7 cms. from the diamond screen. The whole tube was carefully exhausted, so that there should be no absorption of the particles before reaching the screen.

The number of scintillations in a given time was counted, and the area A of the aperture in the brass plate, and its distance R from the polonium, carefully determined. If n is the number of particles hitting the screen in a time t

seconds, then the number of particles emitted by the polonium per second across a hemisphere drawn about its upper surface is

$$N = \frac{2\pi R^2}{A} \cdot \frac{n}{t},$$

assuming that the particles are given out equally in all directions. This assumption was verified by Rutherford in a separate experiment. For the disc used by Regener N was found to be $3{\cdot}935 \times 10^5$.

To measure the total charge carried by the α-particles from the disc a Faraday cylinder was used. This consisted of a partially closed brass cylinder F (Fig. 7, *b*) enclosed in a glass chamber exhausted to a very high vacuum to avoid any loss of charge by ionisation in residual air. The polonium was mounted at P, so that the α-particles from its upper surface entered the cylinder. Here they gave up their charges to it, gradually raising it to a positive potential, which could be measured by an electrometer or electroscope connected to the metal electrode E.

The method of measuring small currents by the electrometer is one in everyday use in this class of experimental work and deserves a little further consideration. Let C be the electrical capacity of the Faraday cylinder and its connections, and suppose the cylinder is placed at zero potential by connecting it to earth. Insulate and note the reading after some suitable interval of time, say *t* seconds. Let V be the potential corresponding to this reading; this can easily be determined by calibrating the instrument with suitable known potentials. The charge given to the electrode in the time *t* is then CV, so that the current between P and F is CV/*t*.

Since the capacity of the system can be made very small the method is far more sensitive than the most delicate galvanometer. The capacity of an electroscope of the C. T. R. Wilson type with its electrode and all its connections need not be greater than 4 or 5 cms., or, say,

5×10^{-12} farads. The electroscope will easily give a deflection of 100 divisions for a potential of 1 volt, while a movement of the gold leaf of a division per minute can be detected with certainty. This corresponds to a current of 10^{-15} amperes. The best galvanometers give a perceptible deflection for a current of about 10^{-11} amperes. The electroscope method is, therefore, about ten thousand times as sensitive as the most delicate galvanometer.

In the present case the value of CV/t gives the charge carried by the α-particles per second from the upper surface of the polonium disc. In electrostatic units it was found to be ·000377. This was the charge carried by the $3{\cdot}935 \times 10^5$ α-particles emitted by the polonium. The charge on each particle was therefore $\cdot 000377/3{\cdot}935 \times 10^5$ or $9{\cdot}58 \times 10^{-10}$ in electrostatic units. Rutherford's value was $9{\cdot}30 \times 10^{-10}$ in the same units.

It will be seen that the mean of these numbers is almost exactly twice the value $4{\cdot}77 \times 10^{-10}$ e.s.u., which represents the best value for the electronic charge e. The charge on the α-particle is therefore twice the charge on the electron. The α-particle is therefore an atom which has lost two electrons. This applies to all the α-particles emitted by radioactive substances which differ from each other only in velocity.

We have stated that the α-particle is an atom: the question arises of what element is it an atom? The ratio of the mass to the charge can be determined for the α-particle in the same way as for the electron, neglecting the different experimental arrangements required. No great accuracy has, however, been reached, as the deflection of the α-particles from radioactive substances even in the strongest magnetic fields is small. According to Rutherford, the ratio of mass to charge for the α-particle from radium is $1{\cdot}97 \times 10^{-4}$, and we have seen that it carries a double charge, or, in the language of electrolysis, is divalent. The electro-chemical equivalent of hydrogen is 10^{-4}, so that if we can assume that the ion in solution carried the electronic charge e, the atomic weight of the

α-particles would be 3·84, which is very near 3·96, the atomic weight of helium. Conversely, if we can show that the α-particle is an atom of helium we shall have direct evidence that our assumption that the monovalent ion in solution carries the same charge as an electron is correct.

The proof of the nature of the α-particle has been given by Rutherford, to whom we owe so much of our knowledge of these rays. The experiment is based on the fact that the α-rays, owing to the great speed with which they are projected by the parent molecule, are able to pass through thin sheets of solid substances which are perfectly impervious to the molecules of ordinary gases.

The substance used as the source of α-particles was radium emanation, the radioactive gas which is the first decomposition product of radium, and on which it is now proposed to bestow the name of radon. This gas, which is disengaged from solutions of radium in water, after being purified in various ways, is finally passed into a fine thin-walled glass tube, the end of which has been carefully sealed. This is enclosed by a wider thick-walled glass tube which is also made quite air-tight and has in its upper portion two electrodes. The spectrum of the discharge between these two electrodes enables us to determine the nature of the gases in this outer tube. There is no connection between the inner and outer tubes, so that nothing can pass from the one to the other, except the α-rays. This point was tested by filling the inner tube with helium and allowing the apparatus to stand for some days. No trace of the helium spectrum was obtained in the outer tube under these circumstances. When, however, the inner tube was filled with emanation, the α-particles emitted were able to pass through the thin glass walls, and, being stopped by the thicker tube beyond, collected in the space between the two tubes.

Slowly, as the experiment went on, the spectrum of helium began to appear, becoming brighter and more complete as more and more of the rays passed through the

inner tube, until at the end of a few hours the complete helium spectrum was obtained. The blank experiments were far more in number and severity than has been described here. They left no doubt that the α-particles were indeed atoms of helium, differing from the ordinary atoms of gas only in their velocity and charge. We have seen above that this result leads directly to the conclusion that the charge on a monovalent ion in a solution is the atom of electricity which we denote by e.

This is one of the most direct proofs of this very important fact. There are, however, many others of very diverse natures, some of which we shall have occasion to discuss when dealing with the phenomena on which they are founded.

The charge carried by a monovalent ion in solution and the electronic charge are thus the same; the value for the latter is, as we have seen, very near $4{\cdot}77 \times 10^{-10}$ e.s.u., or $1{\cdot}59 \times 10^{-20}$ in electromagnetic units. The ratio of the mass to the charge for the hydrogen atom in solution is, as we have seen, $1{\cdot}04 \times 10^{-4}$. Thus the mass of the hydrogen atom is $1{\cdot}04 \times 10^{-4}\, e$, or $\mathbf{1{\cdot}66 \times 10^{-24}}$ **gms.** This is therefore the value in grammes of the chemical unit of atomic weight, and we can at once calculate from it the actual mass of any atom of which the chemical atomic weight is known. The accuracy of the result depends only on the accuracy with which the value of e can be determined. A reference to Table II. (p. 25) will show that the error in the value we have used probaby does not exceed 1 per cent. at most. In fact Millikan claims that his result is not in error by more than 1 part in 1,000.

Since the mass of a cubic centimetre of hydrogen at normal temperature and pressure is almost exactly 9×10^{-5} gms., the number of hydrogen atoms contained in 1 c.c. of a gas under these conditions is $9 \times 10^{-5}/1{\cdot}66 \times 10^{-24}$, or $5{\cdot}4 \times 10^{19}$. The number of molecules in 1 c.c. of hydrogen gas is therefore $2{\cdot}70 \times 10^{19}$. By Avogadro's hypothesis this number is independent of the nature of the gas.

CHAPTER IV

POSITIVE RAY ANALYSIS

We have considered so far the case of the positively charged particles from radioactive substances, and have seen how their mass, charge and chemical nature have been determined, and how these determinations have given us the most certain and accurate estimate of the actual mass of a hydrogen atom. The information obtainable was, however, limited by the fact that these particles are all of one kind, consisting always of atoms of helium.

We have already mentioned that it is possible, in a discharge tube, to endow atoms and molecules of ordinary matter with those properties of high velocity and electric charge which have made the α-particles so amenable to experiment. Owing to the magnitude of the electric field the positively charged ions, which are produced in large numbers by the discharge, are propelled with high velocities towards the cathode, forming what is known as the *positive rays*.

If the cathode is suitably perforated, the positive particles will pass through it, and emerge on the further side with their velocity unimpaired. They can then be detected by allowing them to fall either on a fluorescent screen, or preferably on a photographic plate, where they will produce a permanent record, which can be measured at leisure with suitable instruments of precision.

The experiments, for reasons to which we have already alluded, presented many difficulties. It was only after several years of experiment that Professor Sir J. J. Thomson at last perfected an apparatus which allowed

him to measure these particles with accuracy and certainty.

A general idea of the apparatus can be obtained from Fig. 8, which is reproduced from a photograph of one of Professor Thomson's tubes. The details are shown more clearly in the accompanying diagram, Fig. 9, which repre-

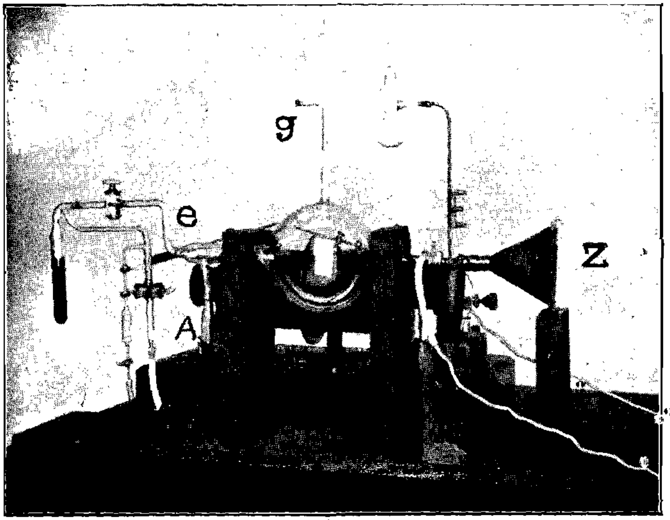

Fig. 8.—Thomson's positive ray apparatus.

sents a section of part of the apparatus as seen from above.

The apparatus consists of two parts: the discharge tube proper, where the particles are produced, and the "camera," where their presence is detected and their masses determined. The discharge tube proper consists of a large bulb T, some 30 cms. in diameter. The anode A (Fig. 8) is placed in a side tube, while the cathode C (Fig. 9) occupies the neck of the bulb. The gas to be experimented on enters the bulb through the tubes at *e*, and is removed through the tube *g* by a Gæde pump,

which is worked sufficiently rapidly to keep the gas in T at a suitably low pressure.

The cathode C (Fig. 9) is an aluminium rod pierced with a very fine copper tube about 8 cm. long and less than $\frac{1}{10}$ mm. in diameter. An exceedingly fine pencil of positive rays is thus obtained. It is evident that with a tube so narrow any stray magnetic field will cause the particles to hit the walls of the tube and be lost. To prevent this the copper tube is enclosed for the greater

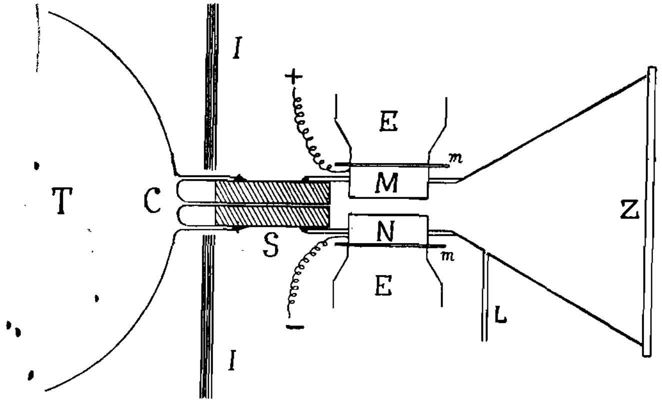

FIG. 9.—Thomson's positive ray tube.

part of its length in a thick iron tube S, shaded in the diagram, while thick iron screens I, I, protect the main discharge from the influence of the magnet.

Owing to the intensity of the discharge the cathode becomes very hot, and it is necessary, in order to protect the numerous sealing-wax joints, to surround them with a water cooling jacket, as shown in Fig. 8.

On leaving the copper tube, the rays pass between M and N, two soft iron blocks let in through the sides of the tube (which is here made of ebonite) and carefully waxed round, so as to be completely vacuum tight. These blocks serve two purposes. In the first place they form

the pole pieces of the electro-magnet E, E, from which, however, they are electrically insulated by two thin sheets of mica, *m*, *m*. This insulation enables them to be charged positively and negatively respectively, by means of a cabinet of small storage cells, and thus to serve as electrodes for the application of an electrostatic field.

In this way the positive particles can be subjected at the same time to a magnetic and an electric field. It will be noticed that, whereas in the case of the cathode ray experiments described in an earlier chapter the two fields were at right angles to each other, in this case the two fields are parallel, and the corresponding deflections therefore at right angles to each other.

After passing through these fields, the rays fall either upon the glass plate Z, which is covered with powdered willemite, or upon a photographic plate, which can be introduced, when required, immediately in front of Z by suitable devices.

The side tube L leads to a tube filled with charcoal and immersed during the experiment in liquid air, a device due originally to Sir James Dewar, for absorbing as completely as possible the gases in this part of the apparatus. This detail, apparently insignificant in itself, has had much to do with the success of the method. If the gas in the camera is at the pressure most suitable for the production of positive rays in the discharge tube, the effects observed on the screen are found to be almost entirely secondary. The residual gas in the camera becomes strongly ionised by the action of the positive rays upon it. The latter are thus travelling through an atmosphere charged with negative electrons, with which they readily combine to form neutral molecules again. When this has taken place, the particle is no longer acted upon by electric or magnetic fields. The exact extent of its deflection will depend upon the length of time during which it has succeeded in retaining its charge. These secondary effects still make their appearance upon some of the photographs taken. They can, however, always be detected by the fact that they

either disappear or alter in position or appearance if the pressure in the camera is slightly lowered or slightly raised.

The charcoal and liquid air method enables us to remove the residual gas so rapidly that it is possible to have the

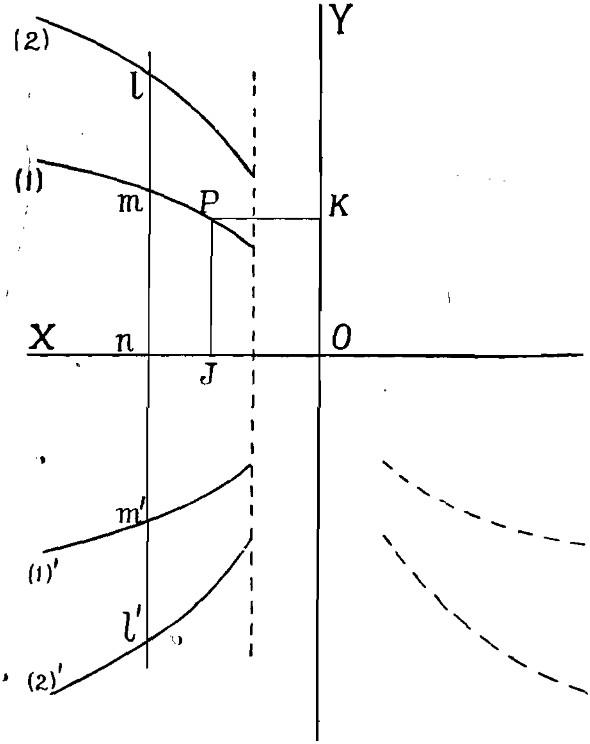

FIG. 10.—Positive ray parabolas.

pressure in the camera considerably lower than that in the discharge tube, the diffusion along the narrow copper tube, which is their only connection, being comparatively slow. In this way the production and the measurements of the particles can both be carried on under the most favourable conditions.

Let us consider the course of the positive particle from its genesis in the discharge tube to its stoppage on the photographic plate. Particles formed near the anode will fall through practically the whole of the difference of potential between the electrodes of the discharge tube, some 30,000 or 40,000 volts. The energy they acquire will thus be V × E, where V is this difference of potential, and E the charge on the particle. Their velocity v, on reaching the cathode, will thus be given by

$$v^2 = 2 \,.\, \mathrm{VE}/m \qquad . \quad . \quad . \; (4)$$

This is the maximum velocity the particles can attain. Those commencing their existence nearer the cathode than this only fall through a fraction of the full potential V, and thus acquire only a fraction of this maximum velocity. Thus, the stream of rays passing through the cathode will contain particles moving with all velocities up to a certain maximum.

On passing into the electric and magnetic fields at MN they will be acted upon by forces equal to XE and HE v respectively, where X is the electric and H the magnetic field, exactly as in the case of the cathode particles, the only difference being that the directions of the deflections will be in the opposite directions to those of the negative particles. It can be shown* that these forces will cause the point at which the particle strikes Z to be deflected through distances equal to $k_1 \dfrac{\mathrm{HE}}{mv}$ in the case of the magnetic field, and $k_2 \dfrac{\mathrm{XE}}{mv^2}$ in the case of the electric field, k_1 and k_2 being constants which depend only on the relative dimensions of the various parts of the apparatus. It must be remembered that the fields have been so disposed that these two deflections will take place at right angles to each other.

Thus if O (Fig. 10) represents the position on the plate

* Appendix A.

of the undeflected rays, and OX, OY are the directions of the electric and magnetic deflections, the particle, after passing through the two fields, will be deflected to some point P such that

$$PK = x = k_2 \frac{X.E}{mv^2} \quad \text{(electric deflection)} \quad . \quad . \ (5)$$

$$PJ = y = k_1 \frac{H.E}{mv} \quad \text{(magnetic deflection)} \quad . \quad . \ (6)$$

We see from these equations that

$$y/x = \left(\frac{k_1}{k_2}\frac{H}{X}\right).v. \quad . \quad . \quad . \quad . \quad . \ (7)$$

$$y^2/x = \left(\frac{k_1{}^2}{k_2}\frac{H^2}{X}\right)\frac{E}{m} \quad . \quad . \quad . \quad . \quad . \ (8)$$

If the strengths of the two fields are kept the same throughout the experiment, all the quantities within the brackets will be constant. Thus, y/x will be a measure of the velocity of the deflected particle, while the ratio y^2/x will measure the ratio of the charge to the mass.

If all the particles were identical, and had the same velocity, the spot O would simply be shifted to the point P. As we have seen, the velocities of the particles vary considerably. The rays will therefore not be deflected to a single spot, even if their mass and charge are identical, but will be drawn out into a line or band. By equation (8) all the particles for which E/m is the same will, however, lie on some curve for which the value of y^2/x is constant; such a curve is known as a parabola.

If the particles emerging from the cathode differ in mass, they will be sorted out into a series of parabolas one above the other, each curve corresponding to some definite value of E/m. Since the velocity which is proportional to y/x cannot exceed a certain value, these curves will not be complete, but will stop short at some definite distance from the axis OY. The appearance of the plate after exposure should therefore be somewhat as shown in the

top left-hand quadrant, Fig. 10, where two such parabolas are shown.

To measure the curves, drop any perpendicular on OX,

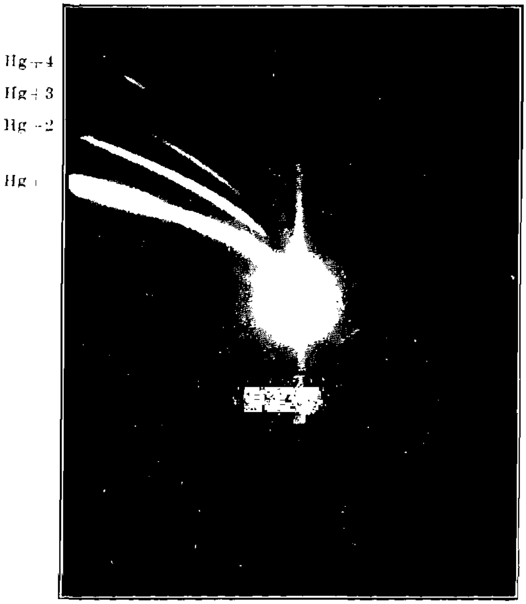

FIG. 11.—Parabolas due to multiple-charged mercury atoms.

cutting the curves in l and m, and the axis in n. Then, from equation (8) it can be seen that

$$ln^2/mn^2 = y_2^2/y_1^2 = \left(\frac{E_2}{m_2}\right) \div \left(\frac{E_1}{m_1}\right)$$

since the value of x is the same for all points along the line mn. Thus, if $E_1 = E_2$, that is to say, if the two particles carry the same charge, the ratio of the masses of the two sets of particles is inversely proportional to the square of their distance from OX.

The line OX has no real existence on the plate, but the

apparatus can be arranged so that the direction of the deflections are parallel to the edges of the photographic plate, while the position of O is always marked by a very bright spot caused by rays which come through the cathode uncharged, and are therefore undeflected. A

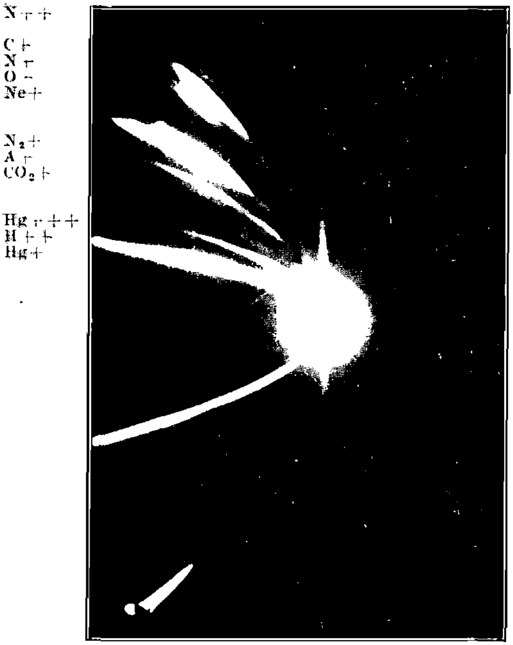

Fig. 12.—Typical positive ray photograph. Atmospheric nitrogen.

more accurate method is to reverse the magnetic field halfway through the exposure. The direction of the deflection is thus reversed, and symmetrical parabolas are formed on the opposite side of OX as shown in Fig. 10. The distance between the two branches of the same curve is then twice the distance of either from the line OX.

It will have been noted that the ratio of the squares on

these ordinates does not give directly the ratio of the masses of the particles, but only the ratio of what we may term their electro-chemical equivalents. Fortunately, however, the majority of the particles carry the single electronic charge *e*, while in any case the charge E on the positive particle cannot be more than a small integral multiple of this. Very little uncertainty is as a rule introduced from this cause, though it does occasionally arise. Mercury is the greatest offender in this respect, as mercury atoms carrying as many as eight charges are sometimes to be detected. Thus, five of the six parabolas on Fig. 11, which is reproduced from one of Professor Thomson's photographs, are due to atoms of mercury, carrying respectively one, two, three, four, and eight charges. The latter line, though clear on the negative, is too faint to show up clearly in the reproduction.

TABLE III.—ATMOSPHERIC NITROGEN

Potential across discharge tube, 30,000 volts; current through magnet, 3·5 ampères; potential difference in electric field, 200 volts.

d mm.	*m*/E.	Probable cause of line.	
7·2	200	Hg +	Mercury atom with single charge.
10·3	100	Hg + +	Mercury atom with two charges.
12·4	67	Hg + + +	Mercury atom with three charges.
15·4	44	CO_2 +	Molecule of carbon dioxide.
16·5	39	A +	Argon atom (40) with single charge.
19·4	28	N_2 +	Nitrogen molecule with single charge.
23·1	20	Ne +	? Neon with single charge.
25·6	16	O +	Atom of oxygen with single charge.
27·6	17	N +	Nitrogen atom with single charge.
30·0	12	C +	Carbon atom with single charge.
38·7	7	N + +	Nitrogen atom with two charges.

The measurement and interpretation of the results can best be illustrated by an actual example. Fig. 12 represents a fairly typical photograph obtained with the

apparatus. The gas in the discharge tube in this case was atmospheric nitrogen, that is to say, air from which the oxygen had been extracted. Table III. contains the actual measurements made on this plate.

The first column gives the distance of the different parabolas from the axis OX, measured along some common ordinate as explained above. The second column gives the value deduced from these figures for the relative masses of the particles, assuming that they all carry the same charge. If the charge carried is double or treble this value, the corresponding mass so obtained will be half, one-third and so on, of the actual mass of the particle. The standard line on this plate was the innermost one of all, which, as its appearance shows, is due to mercury carrying a single charge. The mass of this particle is for convenience taken as being equal to its atomic weight (200).

Examining the table, it will be seen that the three inner parabolas represent particles having a value of m/E of 200, $\frac{1}{2}$. (200), and $\frac{1}{3}$. (200). They are due to mercury atoms having, respectively, one, two, and three charges. Mercury vapour is always present in the tube unless special precautions are taken to exclude it, as it is used in the vacuum pumps attached to the apparatus. The next line is made by particles having a mass of 44 ; these are singly charged molecules of carbon dioxide, carbon compounds being usually present as impurities in small quantities.

The argon line (39) is the long bright parabola, immediately below the very thick bright line (28), due to molecules of nitrogen with a single positive charge. This, as might be expected, is the brightest line in the photograph. The parabola for which d is 23·1 is very faint on the reproduction. It probably represents neon (20), though there is also the possibility that it is formed by argon atoms with a double charge, as the argon line (40) is very bright. Our method does not enable us to distinguish between these alternatives.

The triplet of lines which follow is due to atoms of oxygen, nitrogen, and carbon. The last line on the plate indicating a value 7 is the nitrogen atom with a double charge. The hydrogen line, which is nearly always

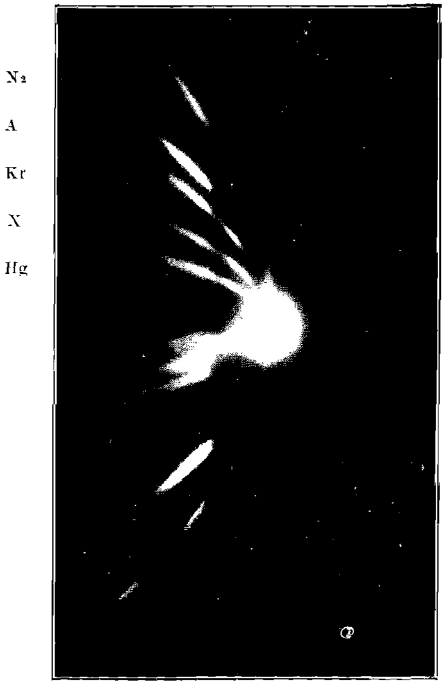

Fig. 13.—Positive ray parabolas.

present, has been deflected entirely off the plate by the large magnetic field applied to separate the heavier constituents.

It will thus be seen that all the lines on our plate correspond to elements which we might expect to find present from the nature of the gas employed. There are no lines unexplained, and the values obtained for the

relative masses of the particles correspond very closely to the atomic and molecular weights determined from chemical considerations.

The faint lines seen on Fig. 12 joining some of the parabolas to the origin are due to the secondary effects which we have already mentioned. The mercury parabolas, however, as will be seen from the figure, do actually extend to within a very short distance of the origin. This is due to quite a different cause. Turning back to equation (5), it will be seen that the electric deflection is proportional to the charge E_1 carried by the particle in the electric field divided by $\frac{1}{2}mv^2$, the kinetic energy of the particle. We have seen that the maximum value of the latter is equal to $V \cdot E_2$, where V is the potential of the discharge, and E_2 the charge carried by the particle in the discharge tube. The minimum value of the electric deflection, that is to say, the nearest point to which the parabolas can extend, will be proportional to E_1/E_2, and will thus be the same for all particles, whatever their mass and charge, if each particle carries the same charge in the tube as in the camera. Thus all the curves will stop short at a certain line drawn parallel to OY. This is well shown in Figs. 13 and 14.

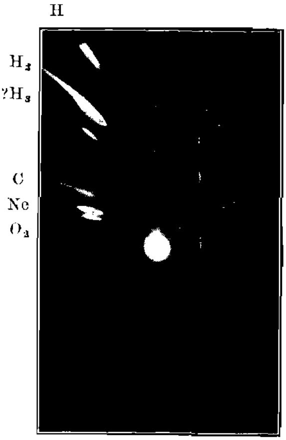

FIG. 14.—Gas evolved from platinum.

If, however, a particle in the discharge tube having a double or treble charge loses one or more of these extra charges before the electric field at MN is reached, the value of E_1/E_2 will be greater than unity, and the parabola will extend further towards the axis OY.

These extensions of the parabolas are very clearly

shown in the three inner curves of Fig. 13, where an almost complete break occurs between the termination of the original parabola and its continuation by particles which have parted with one of their original charges. These three parabolas are due respectively to mercury (200), xenon (132), and krypton (83). The two outer curves, representing argon (40) and the nitrogen molecule (28), end abruptly at the normal distance from OY.

The best example of the effect is, however, shown by the mercury lines in Fig. 11. The normal mercury atom in the discharge tube apparently carries a charge of $8e$, and approaches the cathode with an amount of energy equivalent to this. The innermost mercury parabola (Fig. 11) gives a value for the mass just 200 times that of the hydrogen atom. It is therefore due to a mercury atom carrying a unit charge, and having thus only one-eighth of the charge it carried in the discharge tube. The value of E_1/E_2 is thus $\frac{1}{8}$, and the parabola extends to one-eighth of the usual minimum distance from the vertical axis. The next line ($m = 100$) is due to atoms with two charges, and extends to one-quarter of the usual minimum distance, and so on, until the last parabola, which corresponds to a mercury atom with eight charges (the same number as in the discharge), ends up at the usual distance from the axis.

This gradual shortening of the parabolas for the differently charged mercury atoms is beautifully shown in Fig. 11, where the terminations of the five mercury parabolas can be seen to lie exactly on a straight line through the point O inclined at an angle to OY, as would be expected on the above theory.

It will be noticed that the lines decrease in intensity as the number of charges carried is increased. This is always to be observed on the photographs, and is a fact which sometimes helps us to the right interpretation of a doubtful line in a photograph. For example, if the line indicating a mass of 20 on Fig. 12 had been brighter than the argon line (40) we should have been able to say

definitely that it was due to atoms of neon, and not to argon atoms with a double charge.

The plates so far described were all taken using large magnetic fields in order to obtain a suitable dispersion of the heavier atoms. The last plate of the series (Fig. 14) was taken with a smaller magnetic dispersion, and shows the lines due to some of the lighter elements. It is of peculiar interest at the present moment, as it is one of the photographs which shows the mysterious line due to particles for which the ratio of the mass to the charge is exactly three times that for the singly charged hydrogen atom. On this account it may perhaps be of interest to give the actual measurements made on this plate (Table IV.). The first column of the table gives the actual measurements of a common ordinate of the different parabolas, the second column the corresponding values of m/E, the ratio for the hydrogen atom being taken as unity.

The gas used in the experiment was a sample of that mysterious gas which is evolved in considerable quantities when any metal is heated, or better still, as in the present case, bombarded with cathode rays in a vacuum tube. That gases were evolved under these circumstances had been known for some considerable time, but their analysis

TABLE IV.—GASES EVOLVED FROM PLATINUM BOMBARDED WITH CATHODE RAYS FOR SIX HOURS

(See Fig. 14)

d mm.	*m*/E.	Probable cause of line.
27·0	1·00	H + Hydrogen atom.
19·1	2·0	H_2 + Hydrogen molecule.
15·6	3·0	? Unknown element.
7·8	12	C + Carbon atom.
6·7	16	O + Oxygen atom (very faint).
5·8	21	Ne + Neon atom (20).
4·8	32	O_2 + Oxygen molecule.

had not been previously effected. As will be seen from

the table, the gas consists principally of hydrogen, but helium and neon are also present, while the plate also shows traces of carbon and oxygen, probably due to impurities in the apparatus.

In addition to these known substances there is also very clearly marked a line, the third from the top of the plate, which cannot be assigned to any known element or compound. There was at first the possibility that it might be due to a carbon atom carrying four elementary charges, but this hypothesis was found to be untenable. In the first place the line under consideration is much brighter than that due to the singly charged carbon atoms, whereas we have seen that on a given plate the curves due to multiply charged atoms are invariably fainter than those due to atoms of the same substance having a single charge. In the second place, when precautions were taken to exclude carbon compounds from the apparatus the carbon line (12) completely disappeared, while the line 3 remained as bright as ever.

Only two possibilities remain. The line may be due to a previously unknown element of atomic weight 3, or it may be due to a hitherto unknown modification of hydrogen H_3 corresponding to ozone. The latter hypothesis has been recently proved to be the correct one by chemical methods.

Another parabola, which first made its appearance when the gases from liquid air residues were introduced into the discharge tube, has led to one of the most sensational of the recent discoveries in science. This is a line giving a value for m/E of 22. This line, which always appears when neon is present in the tube, might conceivably have been a molecule of carbon dioxide (44), with a double charge. This suggestion was, however, negatived by the fact that the line could be obtained even when the CO_2 and the CO lines were completely absent. The matter was pursued vigorously by Aston, who showed that the substance giving this line could not be separated from neon by any chemical process. By an ingenious modifi-

cation of the arrangement of the two fields he was able to use slits still finer, and dispersions still greater than those employed by Sir J. J. Thomson. In fact so great was the dispersion that the lines of two elements differing only by unity in atomic weight could be separated by as much as a centimetre on the photographs. It was possible, therefore, to measure the relating masses of the particles with an accuracy approximating to one part in 1,000, an accuracy comparing not unfavourably with many determinations of atomic weight by chemical methods.

It was then discovered that many of the parabolas which, at the lower dispersions, had been taken for single lines were in reality doublets, like the neon line and its satellite. When chlorine, for example, was introduced into the discharge two lines appeared on the plate, one corresponding to a mass of 35, and the other to a mass of 37. There was no line corresponding to 35·4, the accepted atomic weight of chlorine. It is impossible to resist the conviction that the element "chlorine" is not a single substance, but consists of a mixture of two gases differing by two whole units in atomic weight. The "atomic weight" given in chemical tables is thus only a sort of average for the two substances. The constancy of this average, which has been verified many times by experiments of the highest accuracy, shows that the proportion of the two substances must remain constant no matter how the chlorine is treated. The two substances must therefore be identical in the chemical behaviour.

The existence of such substances, which differ in atomic weight, but possess identical chemical properties, had been suggested by Soddy from a study of the radioactive elements, which we shall have to deal with later in the volume. In fact, it seemed impossible to find place for the thirty-five new radioactive elements in the few remaining spaces in the Periodic Classification Table on any other hypothesis. For such pairs of substances he proposed the name Isotopes, which has been generally

accepted. Aston's work has conclusively shown that isotopes are not confined to radioactive elements. Argon, for example, consists of two isotopes of atomic mass 36 and 40; bromine is also a mixture of two kinds of atoms with masses of 79 and 81, while krypton consists of a mixture of no less than six isotopes with masses 78, 80, 82, 83, 84, and 86. On the other hand, elements such as oxygen, nitrogen, carbon, and fluorine, are pure substances. It is noteworthy that within the accuracy of the experiments, which, as we have seen, is very considerable, every atom has a mass which is exactly an integer if the mass of the oxygen atom is taken as 16. Elements whose atomic weights on this basis were known to be whole numbers have been found to be pure substances, while elements whose chemical atomic weights were not exactly whole numbers have been found, when examined, to consist of mixtures of isotopes, the masses of which are exact whole numbers. We are thus thrown back again on the hypothesis of Prout, that all elements are compounded of definite numbers of atoms of one primordial substance.

The one certain exception so far recorded is curiously enough hydrogen itself, which has been found by Aston to have a mass of 1·008, as compared with 16 for oxygen. This, of course, confirms the results obtained by chemical methods. We shall return to this point in a later chapter.

A few further points of interest in the photographs may be noted. The bright central spot shown in all the figures is due to the particles which have lost their charge during their passage through the long copper canal tube, and are therefore undeflected by any combination of electric and magnetic fields. The atoms of some elements have such a strong attraction for the surrounding negative electrons that they actually take up more of them than would be sufficient to neutralise the original positive charge. They thus enter the deflecting fields with a negative instead of a positive charge, and so give rise to para-

bolas in the opposite quadrant to those due to the positive particles, but giving, of course, the same values for m/E. Oxygen and the halogens if present in any quantity almost invariably give these negative curves. Strangely enough hydrogen, which is generally reckoned among the more electro-positive elements, also frequently shows the same effect. It has never been found with nitrogen or helium.

We have so far only been considering the relative values on the ratio m/E for the different particles. By measuring the dimensions of the different parts of the apparatus and calculating the actual values of the constants k_1 and k_2, the absolute value of this ratio for any given parabola can be deduced. Such a determination was made by Professor Sir J. J. Thomson, and it was found that the absolute value for the outermost parabola of all was almost exactly 10^{-4}. We have seen that this is the value of the ratio for a hydrogen ion in solution or a hydrogen atom carrying a single charge. The particles with which we have been dealing are therefore actual atoms and molecules of the substances in the discharge tube, as we have tacitly assumed in the foregoing pages.

We have now described in some detail the principal features of the new method of molecular analysis. Its importance can hardly be exaggerated. In the first place it enables us to detect with certainty the presence in a gaseous mixture of far smaller quantities of an element than could be accomplished by any other method known to science. Professor Thomson has given the following striking illustration of the delicacy of the method. It was found that the photographs taken with atmospheric argon in the apparatus always showed the helium line faint but quite distinct. In this particular experiment the volume of the discharge tube was about 2 litres, and the pressure of the gas in the tube 1/300 mm. of mercury. The gas experimented on would therefore have had a volume of about 1/100 c.c. at atmospheric pressure. This is approximately the quantity of argon in 1 c.c. of air at

atmospheric pressure. We are thus able to detect the helium present in a single cubic centimetre of air. According to the determination of Professor Ramsay this amounts to no more than four-millionths of a cubic centimetre.

The new method has the further advantage over spectroscopic analysis that it gives directly the atomic or molecular weight of the substance under experiment. Thus the photograph of Fig. 14 not only reveals the existence of a new gas but gives at once its molecular weight.

Lastly—and this is perhaps most important of all from the point of view of an intimate study of the modes and methods of chemical combination and decomposition—the time taken for each single particle to register its presence and mass is exceedingly minute. A very moderate value for the speed of the positive particles is 10^8 cms. per second (about 620 miles per second). Their path in the discharge tube is not more than 50 cms. in all. Thus a particle when caught by the discharge will register itself on the photographic plate in considerably less than one-millionth of a second.

We might therefore reasonably expect to find on the photographs curves corresponding to temporary combinations of atoms so unstable that their whole period of existence is not greater than one-millionth of a second, if any such combinations are formed in the discharge tube. Thus in the case of chemical reactions taking place within the discharge tube we might expect to find on the plate traces not merely of the stable products of the reaction but also of any intermediate stages occurring in the course of the reaction. The field thus opened up for an intimate study of the mechanism of chemical reactions is illimitable.

Though little has as yet been accomplished along these lines, the experiments already made show that this expectation is not unfounded. As a very simple illustration of the application of the method we may take the

case of phosgene, $COCl_2$. When this was introduced into the apparatus the photographs showed that, in addition to the molecules of undecomposed phosgene (99), the carriers of positive electricity were molecules of carbon monoxide (28) and atoms of chlorine (35·5). The lines due to single atoms of carbon and oxygen were very faint indeed, thus showing that the decomposition of the compound by the discharge consisted of the separation of the chlorine atoms from the CO molecule, the bond between the carbon and oxygen atoms remaining intact.

This is a simple case where the results obtained might easily have been predicted. Another interesting case is that of methane, CH_4. When this gas is subjected to the discharge a group of five lines appears on the photographic plate, indicating the presence of particles having masses 12, 13, 14, 15 and 16 times that of the hydrogen atom. These correspond to particles having the composition C, CH, CH_2, CH_3, and CH_4 respectively.

One word may be added as to the relative intensity of the different lines on a given photograph. It is found that in general this is far from representing the actual proportion of the particles in the stream having masses corresponding to the different lines. For some reason at present unexplained, a given number of atoms of a light element produce far greater effect on a photographic plate or willemite screen than an equal number of the atoms of a heavier element. Thus the parabola corresponding to the hydrogen atom will often be the most intense line on the plate when the amount of that element present forms less than 1 per cent. of the contents of the tube.

This has been very clearly demonstrated by Sir J. J. Thomson by substituting an electrical for a photographic method of detecting the positive particles. It must be remembered that as all the particles with which we are dealing carry an electric charge, they can be detected by collecting them in a Faraday cylinder in the way described for the α-particles in the preceding chapter.

To carry out the experiment a brass plate B (Fig. 15) was substituted for the glass screen Z of Fig. 9. If the brass plate is covered with powdered willemite a series of bright parabolic curves will of course appear upon it when the tube is running somewhat as indicated in Fig. 15A, where three such curves are shown. If a slit SS is cut in the brass plate, so as to coincide with one of the parabolas, the particles forming this parabola will pass through the slit and can be collected by a Faraday cylinder F (Fig. 15B) placed immediately behind it. As explained in Chapter III. the rate of charging up of an electrometer connected to the Faraday cylinder will be proportional to the number of particles entering the latter per second, that is to say, to

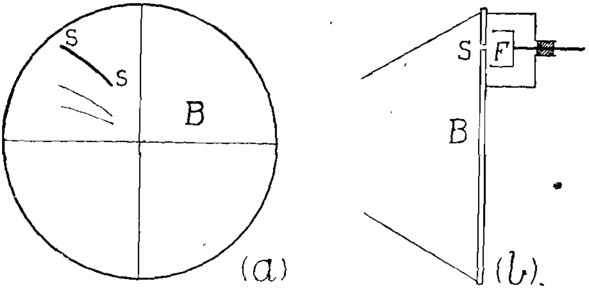

FIG. 15.—Apparatus for the electrical measurement of the positive rays.

the relative number of molecules in the positive rays which have a mass corresponding to that indicated by the parabola coinciding with the slit SS.

If the slit could be made to coincide successively with each of the different parabolas indicated by the glowing willemite, the relative rates of deflection of the electrometer for the different positions would be proportional to the number of particles of corresponding mass in the positive rays from the discharge. The experiment can be performed much more conveniently without moving the slit by varying the intensity of the deflecting magnetic

field, H. If this is increased it can easily be seen that the corresponding magnetic deflections of the particles will also be increased and the various parabolas will move outwards from the centre of the screen. In this way each of them in turn can be brought to coincide with the parabolic slit SS. It can easily be seen from equations (5) and (6) that if the other conditions of the experiment remain the same the value of m/E for a given set of particles is proportional to the square of the strength of the magnetic field necessary to deflect them to a given position. Thus from the various rates of deflection of the electrometer corresponding to different values of the magnetic field we can at once determine the relative number of particles in the beam of positive rays corresponding to definite values of the ratio m/E. In other words, we can determine the relative proportions of the different kinds of atoms and molecules which make up a given beam of positive rays.

On making the experiment it was found that there was practically no movement of the needle of the electrometer connected to the Faraday cylinder except when one of the bright parabolas was made to coincide with the slit. If a fairly narrow slit was used, the appearance and disappearance of a deflection of the electrometer as such a line passed across the slit was surprisingly sharp, and lines quite close together could easily be distinguished.

Although we can thus perform a quantitative analysis of the beam of positive rays, it cannot be assumed without further experiment that the number of atoms of an element in the beam is necessarily proportional to the quantity of the substance present in the discharge tube. Preliminary experiments, however, seem to indicate that this is very approximately the case, at any rate for the non-metallic elements. (Metallic elements, with the exception of mercury, exhibit an unaccountable reluctance to enter the positive stream and can only be made to do so by heating their compounds to a high temperature on the anode.) If so, this latest modification of the method of

molecular analysis will enable us to carry out not merely a qualitative but also a quantitative analysis of any gas introduced into the discharge tube. The quantitative determination of traces of a gaseous substance too small to be detected by the spectroscope will then have become an accomplished fact.

CHAPTER V

THE NATURE AND SIZE OF AN ELECTRON

We must now turn from these triumphs of experimental skill to some theoretical considerations, and discuss briefly the new views of the atom to which they have given rise. It would be idle to pretend that we have as yet any theory of the structure of the atom which absolutely and completely sums up all the known phenomena of science. The scientific philosophers of an earlier age hoped that at no very distant date they might be able to include in one or more ponderous tomes all that could be known in the realm of physical phenomena. Looking down the long vistas which the new discoveries have so recently opened up, we expect no such immediate end. We are not yet within sight of a mechanical or electrical theory of the universe wherein all the chemical and physical properties of the material universe shall be explicable in terms of the electrons and their motions. Still, while we cannot say that we have such a theory, there are certain sign-posts pointing out the direction in which we may hope for ultimate success. Even now it is possible to construct " models " of the atom which, however crude and insufficient they may be, enable us to link together many most diverse phenomena.

In the realm of science an insufficient, or even a false, hypothesis is better than none at all, and it will be useful to take the best approximation we can devise to serve us as a clue through the labyrinth of experimental facts which we have still to consider. At the same time it will be well to point out carefully where we are treading the solid ground of experimental fact and legitimate deduction,

and where we rise to the higher but more precarious flights of scientific imagination.

We have seen that electrons are contained in all atoms, and many phenomena lead us to believe that they play a most important part in determining both the chemical and the physical properties of the substance. The question naturally arises, What is an electron? Fortunately to this question we are able to give an answer. An electron is an atom of electricity free from association with anything in the nature of matter as we know it. It not merely has a charge, it *is* a charge, and apart from its charge has no existence and no properties, not even that of mass.

The exact proof of this statement has involved long and intricate mathematical analysis. It will, however, be possible, without going at all deeply into these abstruse calculations, to make clear the nature of the proofs advanced, and the experimental evidence upon which they rest.

In the first place, since we have already determined the mass of an electron, we must show that such a moving electric charge will possess mass, a property which we have been accustomed to associate only with what we call matter. The proof follows directly from the ordinary laws of electric and magnetic induction, and was first given by Professor J. J. Thomson in 1881, many years before the discovery of the electron rendered possible any practical application of the result.

Consider a small sphere charged with electricity of either sign moving through space with a velocity v. We have already pointed out that this moving sphere will be equivalent to an electric current element coinciding with the path of the particle. By the usual laws of electromagnetism this current element will produce a magnetic field, at a distance r from the particle, equal to $ev \sin \theta / r^2$, where θ is the angle between the direction of motion of the particle and the direction of r. Thus, the moving particle is surrounded not only by an electrostatic field due to its

charge, but also by a magnetic field due to the motion of that charge. It will be seen that this field has its greatest value in a direction at right angles to the motion of the particle, and falls to zero in the direction in which the particle is travelling.

It is a well-known fact that a magnetic field is the seat of energy, the energy in a field of strength H being $\frac{H^2}{8\pi}$ times the volume. The magnetic energy in a small space of volume u at a distance r from our moving charge is thus

$$\left(\frac{ev \sin \theta}{r^2}\right)^2 \frac{u}{8\pi} \quad \text{or} \quad \frac{ue^2 \sin^2\theta}{8\pi\, r^4} \cdot v^2.$$

The total energy of the magnetic field surrounding the particle is the sum of the energy in all these little volumes, from the surface of the particle away to infinity. The summation of this quantity does not present any difficulties. It is equal to $\frac{1}{3}\frac{e^2v^2}{a}$, where a is the radius of the particle.

If m is the ordinary mechanical mass of the particle, the kinetic energy due to its motion will be $\frac{1}{2}mv^2$. In addition to this there is, as we have shown, a quantity of energy due to its charge. The total energy of the moving particle and its charge is thus

$$\frac{1}{2}mv^2 + \frac{1}{3}\frac{e^2v^2}{a}.$$

If we write this in the form $\frac{1}{2}\left(m + \frac{2}{3}\frac{e^2}{a}\right)v^2$, and compare it with the ordinary Newtonian expression for the kinetic energy of a particle $\left(\frac{1}{2}mv^2\right)$ we see that the particle behaves as if its mass m had been increased by an amount equal to $\frac{2}{3}\frac{e^2}{a}$. This is the extra or "electrical" mass, due to the fact that the particle carries a charge. It is evident

that, even if m, the "mechanical" mass of the particle, is zero, the "electrical" mass due to the moving charge will still persist. Thus, even if our electron is a pure charge unassociated with any mechanical mass, it will still have an electrical mass equal to

$$\frac{2 \times (\text{electrical charge})^2}{3 \times (\text{radius})} \quad . \quad . \quad (9)$$

Since this "electrical" mass is really that of the magnetic field *surrounding* the particle, it resides not in the particle itself but in the medium surrounding it, that is, in that mysterious fluid which we call the ether. As soon, however, as we attempt to alter the motion of the particle this energy flows into it from all sides, so that, as far as experiments upon the particle itself are concerned, the results obtained are precisely the same as if it resided permanently there.

To make this somewhat novel idea a little clearer we may consider a close and very serviceable analogy, where the mechanism of the extra mass is a little clearer than in the electrical case. If any body is moving through water, or any viscous fluid, it carries with it a certain amount of the liquid through which it is moving. In the case of a sphere, for example, the quantity carried along by the motion of the body amounts to half the volume of the sphere itself. A long cylinder moving at right angles to its own length will carry with it a quantity of fluid equal to its own volume. On the other hand, if it moves in the direction of its own length the fluid entangled is practically *nil*. Thus, in order to set the body in motion with a velocity v, we have to supply to it energy enough to give this velocity, not only to the body itself, but also to the mass of fluid which it carries with it. That is to say, if M is the mass of the body itself, and M′ the mass of the attached fluid, the work done in starting the body is $\frac{1}{2}(M + M')v^2$. In other words, the body will behave as if its mass were increased by the mass of the fluid entangled

by it. Just as in the electrical case, this extra mass resides in the surrounding medium, but makes itself apparent at the surface of the body when the motion of the latter is altered in any way.

We may very profitably extend this analogy further in that part of our proof which still remains to be considered, by thinking of our electric field in terms of tubes of electric force. This conception we owe to the genius of

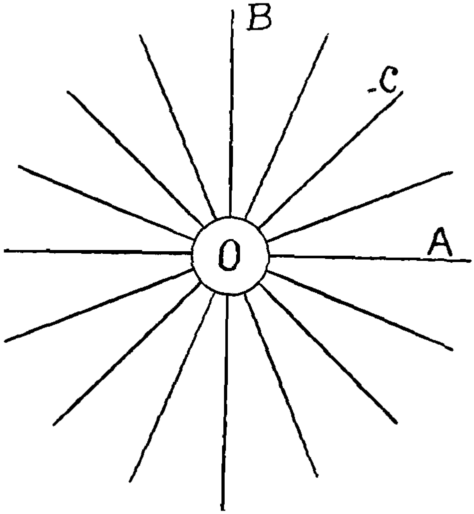

FIG. 16.—Distribution of tubes of electric force round an electron at rest.

Faraday. Untrained in the methods of mathematicians, he found the mere algebraical expression for the laws of electrical attraction both unsatisfying and unstimulating. He felt that if two bodies attracted each other it could only be because of some vital bond between them. Thus he imagined that every positive charge was the beginning of a certain number of tubes of force stretching out through space until, somewhere or other, they ended up on an equal but opposite negative charge.

By assuming that these tubes were in a state of tension

so that they tended to shorten themselves as much as possible, and, further, that two similar tubes repelled each other, he was able to give a clear explanation of the various electrical phenomena. Thus the attraction between two oppositely charged bodies was the result of the tendency of the tubes connecting them to contract; the repulsion between two like charges was due to the mutual repulsion between the tubes of force radiating from each of them. An electric current was the motion of one of the ends of the tubes of force along the conductor, while the magnetic effect in the neighbourhood of the current was due to the motion of the tubes of force through the surrounding medium.

The concentration of attention upon the phenomena of currents which marked the latter half of last century tended to throw somewhat into oblivion this conception of Faraday. The recent researches with which we are dealing have, however, found in it a most powerful weapon, and are tending to give to these tubes of force a definite significance and concrete existence of which even their originator perhaps hardly dreamed.

Let us add to the postulates already made by Faraday this additional assumption, that a tube of force when moving through the ether is able to grip a certain quantity of that subtle fluid, in much the same way that a cylinder carries along with it a definite mass of any liquid through which it moves. For a single charged particle at a considerable distance from all other attracting bodies the lines of force will radiate out in straight lines from its surface, and, if the latter is spherical, the tubes will space themselves evenly around it owing to their mutual repulsion. In section, therefore, they will appear somewhat as in Fig. 16.

Suppose this system to be moving through space in the direction OA with a velocity v. If our analogy with the case of a body moving through water holds, the tubes like OB, which move at right angles to their length, will grip the maximum amount of the ether through which

they are moving, while tubes like OA, which are moving along their length, will carry none. It will thus be seen that the distribution of energy in the field surrounding the particle will correspond exactly with the distribution of energy in the electro-magnetic field of which it is supposed to be a visualisation. The electrical mass of the particle

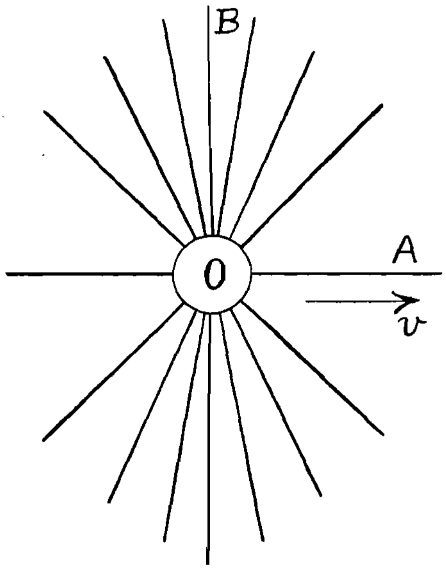

FIG. 17.—Distribution of tubes of electric force round a moving electron.

will then be the whole mass of the ether gripped by these radiating tubes.

Now it is a well-known fact that a cylinder moving through a fluid in the direction of its own length is not in stable equilibrium. In accordance with the well-known principle of least action, the cylinder will tend to turn so as to offer the greatest possible resistance to the motion; that is to say, it will tend to set itself at right angles to the direction in which it is being compelled to move.

Any one who has attempted the art of punting will recall the almost uncanny tendency of the punt to set itself at right angles to the direction in which it is travelling. If this holds for tubes of force travelling through the ether, then tubes like OA are not in stable equilibrium, but will tend to turn into the plane of OB, which we may call the equatorial plane. It can be shown from the principles of electricity that such a tendency does indeed exist. The repulsion between the different tubes will, of course, tend to keep OA in position, and, as this repulsion is very great, at moderate velocities the effect we are considering will be quite negligible. The force, however, tending to displace the tubes increases with the velocity of the particle, so that at speeds approaching that of light there is a very perceptible shifting of the lines of force into the equatorial plane, as indicated in Fig. 17. But we have noted that the mass of ether gripped by the tubes in this position is greater than that which they originally held. Thus we arrive at the somewhat startling result that the electrical mass of a particle is not a constant, but depends —at any rate, at high velocities—upon the speed with which it is moving.

We have followed out the theory of the variation of electrical mass from the standpoint of Faraday's tubes of force, because in the first place it gives us at once a clear and vivid picture of the processes which are going on in the field, while in the second place we are being gradually driven to the conclusion that some such entities do play a very important part in the phenomena of the electric field. The fact of the variation of electric mass with the speed, however, does not depend in the least upon the particular way in which we choose to regard the electric field, but is a direct though obscure consequence of the fundamental facts of science.

The exact relation between the electrical mass of a moving charge and its velocity depends somewhat on the assumptions we make as to the distribution and geometrical configuration of the charge. Thus, starting from

different ideas of the shape of the electron and the way in which its charge is arranged, different mathematicians have arrived at somewhat different formulæ for this relation. Fortunately, when these are reduced to figures the differences between the best of them are so small that our experiments are scarcely accurate enough to settle definitely between them. The formula now generally accepted, which was due originally to Lorentz, and which has received independent confirmation from the theory of Relativity, makes—

$$\frac{\text{electrical mass } m \text{ at a velocity } v}{\text{electrical mass } m_0 \text{ for small velocities}} = (1 - \beta^2)^{-\frac{1}{2}}, \quad (10)$$

where β is the ratio of the velocity of the particle to the velocity of light.

Let us see now how these results assist us to discover the nature of an electron. The total mass of the electron may be made up of two parts: its mechanical mass, which is constant and independent of the velocity with which the electron is moving; and an electrical mass, which increases with the velocity in the way we have just considered. If the electrical mass of the electron is small compared with its ordinary mechanical mass, then there will be very little variation in the total mass of the electron as the speed is increased. If, on the other hand, the whole of the mass is electrical in its nature, the total mass of the electron should increase at the rate given by the formula (10) above. If part of the mass is mechanical and part electrical, the rate of increase of the whole mass of the electron with increasing velocity will be somewhere between these two values.

If we substitute numerical values in the equation given above, it will be found that the difference between m and m_0 is quite inappreciable unless the speed of the particle is very high indeed. Thus, when the velocity is as much as one-tenth that of light, the increase in the electrical mass only amounts to about 1 per cent., while even when the velocity reaches one-third that of light—that is to say,

over 60,000 miles per second—the increase in the mass is only about 5 per cent. As this was about the maximum

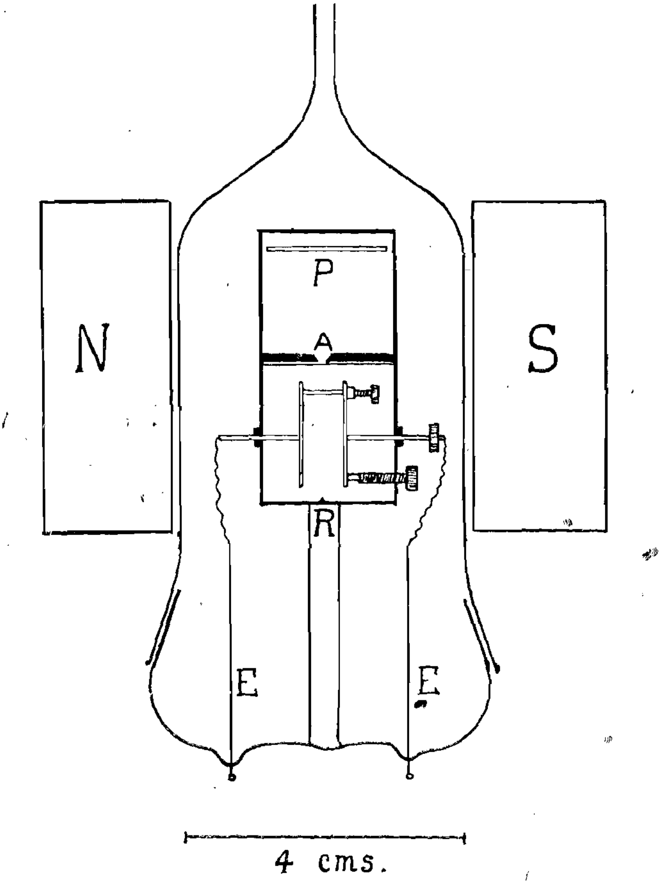

Fig. 18.—Kaufmann's apparatus for determining the mass of a β-particle.

velocity attainable in a discharge tube, it might have been thought that the experimental investigation of the variation of mass with speed lay for ever beyond our reach.

Fortunately this is not the case. Experiments have shown that the β-particles from radium, while otherwise similar to cathode rays, travel with velocities enormously greater even than those of the particles in a discharge

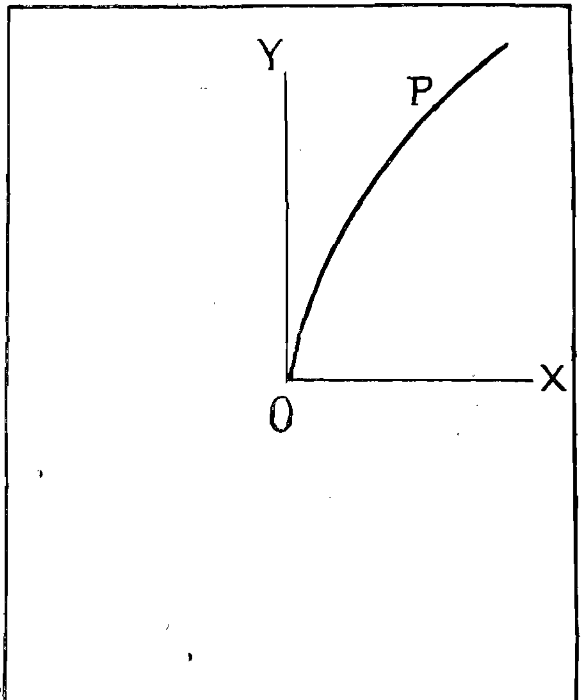

FIG. 19.—Kaufmann's experimental curve for the electric and magnetic deflection of the β-rays from radium.

tube, in some cases approaching within 2 per cent. of the velocity of light itself. For speeds such as this the electrical mass should be more than five times its ordinary value, and thus, by careful experiments on these particles, we might well hope to put to the test the theories we have propounded.

The experiments were first made with exquisite skill and care by Kaufmann. In principle the methods he employed were identical with those already described. The β-particles given out by a small quantity of radium placed at R (Fig. 18), passed through a fine hole in a lead screen at A, before finally falling on a photographic plate at P. Before reaching the hole at A the particles passed between two parallel plates, which could be very carefully adjusted by means of a series of levelling screws, and which were charged to a high difference of potential. The whole of the apparatus was placed between the poles of a strong electro-magnet N, S, arranged so that the electric and magnetic fields were parallel to each other and therefore the corresponding deflections they produced at right angles to each other, exactly as in Professor Sir J. J. Thomson's experiments on the positive rays.

If all the β-particles had the same mass and differed only in velocity, they should be drawn out into a parabola, on the principles already described for the similar experiments on the positive rays. If they consisted of a mixture of different particles the plate should show a series of these parabolas. As a matter of fact Kaufmann's plates showed a single curve (Fig. 19) which, however, was not parabolic but rose less steeply from the origin. This indicates that the particles with the higher speeds were distinctly more massive than those which travelled more slowly. For each velocity there was one, and only one, corresponding mass, or as the mathematicians would put it, the mass of a β-particle is a continuous function of its velocity.

The curve can be measured with a micrometer in the same way as has been described for the positive ray parabolas, and by determining the constants k_1 and k_2 for the apparatus the velocity and the mass of the particles can be determined from equations (7) and (8) of Chapter IV. The experiments have since been repeated by Bucherer with still greater accuracy. On comparing his experimental results with the theoretical relation given by

Lorentz it was found that the maximum divergence was less than 1 per cent. We are, therefore, compelled to conclude that the whole mass of the electron is electrical in origin, and is simply due to its charge. The actual variation in mass of an electron with velocity is indicated in Table V. It may be noted that it follows from the

TABLE V.—VARIATION OF THE MASS OF AN ELECTRON WITH VELOCITY

Velocity of Electron.	β	$\frac{m_v}{m_0}$
3×10^8 cm. per sec.	·01	1·000
3×10^9 " "	·10	1·005
9×10^9 " "	·30	1·048
$1·5 \times 10^{10}$ " "	·50	1·115
$1·8 \times 10^{10}$ " "	·60	1·250
$2·1 \times 10^{10}$ " "	·70	1·400
$2·4 \times 10^{10}$ " "	·80	1·667
$2·7 \times 10^{10}$ " "	·90	2·294
$2·85 \times 10^{10}$ " "	·95	3·203
$2·94 \times 10^{10}$ " "	·98	5·025

formula that the mass of an electron moving with the velocity of light would be infinite. Hence no force, however great, would be able to give to any substance containing electrons a velocity actually as great as that of light.

We have now discussed the evidence for our original statement that the whole mass of the electron is electrical in origin and due entirely to the charge it carries. Granting this conclusion, we can at once determine the dimensions of the electron, and so complete our knowledge of its properties.

We have seen that the electrical mass of a charge e for moderate speeds is equal to $\frac{2}{3}\frac{e^2}{a}$ where a is the radius of the space occupied by the charge. The mass of an electron is $9·0 \times 10^{-28}$ gms., while the value of the charge it carries

is $1 \cdot 59 \times 10^{-20}$ units. Substituting these values in the formula we find that the radius of an electron is $1 \cdot 87 \times 10^{-13}$ cms.

It is, perhaps, only fair to point out that on the Principle of Relativity, all mass, whether electrical in its origin or not, should vary with the velocity in accordance with equation (10). The experimental verification of this formula does not then strictly prove that the mass of the electron is electrical. The conception, however, is one which physicists will not lightly abandon, and we have ample evidence, from other sources, that the radius of the electron, as calculated in this chapter, corresponds very closely to the actual size of this important particle.

We have stated elsewhere that the radius of an atom is of the order of 10^{-8} cms., and have attempted to form some idea of the exceeding smallness of this magnitude. We may now say that small as the atom is, the electron is so much smaller that the electron bears to the atom which contains it very much the same relation as a pea to a cathedral.

CHAPTER VI

THE STRUCTURE OF THE ATOM

THE discoveries which we have been describing at once gave rise to fresh speculations as to the nature of matter and the constitution of the atom. The proof afforded by chemistry that all the myriad substances around us were built up from some seventy or so different elements had indeed effected a very marked reduction in the apparent complexity of the material world, but it had always been felt that the reduction was not sufficient, and that seventy different and independent kinds of atoms was far too many to go to the construction of a well-organised universe. Previous attempts to reduce this chaos to scientific order had languished for want of any kind of experimental basis, though on the other hand the ever-increasing proofs of order supplied by the periodic classification of the elements made it increasingly certain that some structural connection of the closest kind must exist between the different elements. The discovery of the electron and its properties, by affording certain knowledge of at least one of the constituents from which the atoms of the different elements were constructed, opened the way to a fresh flood of daring speculations.

We have seen that the whole mass of the electron may be ascribed to the charge which it carries. The thought at once suggests itself: Are there, indeed, two kinds of mass, or is all mass electrical in its origin? The mass of a negative electron is about 1/1845 part of the mass of a hydrogen atom. Neglecting the positive part of the atom it would require about 1845 electrons to make up the mass of a single hydrogen atom. This, of course, is by no means an impossible number considering the smallness of the electron in comparison with the size of the atom: and specu-

lations along these lines were very freely indulged in for a time. In this case, however, experiment failed to confirm the bold conjecture. As we shall see later, the number of electrons in the atom has been determined, and affords no support for such a theory.

It will be advantageous at this point to divert our attention from the electron to the remaining portion of the atom. In so doing we are departing widely from the historical order of development of our subject. Nearly twenty years elapsed after the discovery of the electron before the other constituent of matter was forced to yield up its secrets, and in the meantime much ingenuity had been expended on the problem of the constitution of the atom. We cannot withhold our admiration from these pioneers, though much of their work has had to be revised in the light of later discoveries, for which their labours paved the way. It will, however, be both shorter and safer to keep to the high road which has now been driven across the places where they groped in the darkness than to attempt to follow them in their wanderings.

Since the electron is negatively charged the remainder of the atom must obviously have a positive charge numerically equal to the sum of the charges on the electrons which the atom contains. The first conception of this positive charge, due to Lord Kelvin, and developed by Sir J. J. Thomson, was that it was uniformly distributed through a sphere of the dimensions of the atom itself. The electrons would then be arranged inside this positive sphere, like the plums in a plum pudding, being kept in their places by balancing against their mutual repulsions the attraction of the positive charge. There were the strongest grounds for assuming that the positive electrification had this form. It had in fact been shown as long ago as the time of Maxwell that, according to well-established electrical laws, it would be impossible to produce a stable arrangement of negative point charges under the action of a positive charge unless the latter were extended in the way assumed; that is to say, unless it occupied a

volume which was large compared with that of the electron. As permanence is, perhaps, the most striking characteristic of the average atom, this assumption of Lord Kelvin's seemed to be the only one possible. We have, however, now obtained the clearest evidence that the assumption is not correct. The hiatus thus created between theory and experiment has not yet been satisfactorily bridged, though, as we shall see later, empirical laws have been formulated by the ingenious Danish mathematician, Bohr, which enable us to deal with the new situation.

Crucial evidence against the Kelvin hypothesis is supplied by experiments on the scattering of a beam of α-rays. The α-particle, as we have seen in an earlier chapter, is an atom of helium, which has lost two electrons, and has been projected with a very high velocity from the atom of a radioactive substance. If a parallel pencil of α-particles is projected through a single thickness of gold leaf the majority pass through without suffering any change of path. A few, however, are deflected through appreciable angles, while about one in every million is so strongly deflected that it actually turns back on its course and emerges from the side on which it entered. Since each α-particle can be made to register itself as a scintillation on a fluorescent screen the experiments can be carried out with considerable certainty and accuracy.

Since the actual mass of an atom of gold can easily be deduced from that of the hydrogen atom, it is a simple matter to calculate the number of atoms of gold contained in a given weight of gold leaf, and it can be shown that the average gold leaf is about 100 atoms in thickness. The fact that it is possible to fire the large majority of the α-particles through such a considerable number of atoms of gold shows that atoms must possess a very high degree of interpenetrability. There can, at any rate, be no sort of solidity about their structure. It is possible, of course, that two positive spheres might be able to penetrate each other, in the way required, but this assumption is incap-

able of explaining the very large deflections which the particles occasionally undergo. The electrical field produced by a positive sphere of electricity reaches its maximum value at the surface of the sphere, falling off to zero as the centre of the sphere is approached. There would thus be a definite maximum value to the force which one positively charged sphere could exert on another, depending on the radii of the two spheres, and the charges which they possess. Now all these factors are, at any rate, approximately known in the case of the helium and gold atoms, and the maximum force which one could exert on the other can be shown to be far too small to produce a perceptible deflection of the α-particle. To account for the very large deflections sometimes observed we must have some system which is capable of exerting during the collision a force far larger than that which could be produced by the collision of two positively charged spheres of atomic dimensions.

If, however, we suppose that instead of being of atomic dimensions the two positive charges occupy a space so small that we can regard them as acting like point charges, the mechanical force between them will be inversely proportional to the square of their distance apart, and will thus increase indefinitely as they come closer and closer together. If we assume that the positive charge on the atom of gold is Ne where N is some whole number, then. since the charge on the α-particle is $2e$ the particles will repel each other with a force $2e \times Ne/d^2$ or $2Ne^2/d^2$ where d is the distance apart. The nearer the two particles approach, therefore, the larger will be the deflection, until in fact an α-particle which was heading straight for the centre of the gold atom would actually be sent back along its own path. All that is necessary is that the sum of the radii of the two particles shall be less than the distance at which the electric force would attain the necessary magnitude.

Since the law of force between the two particles is that of the inverse square of the distance, the problem is mathematically identical with that of two gravitating

bodies, such for example, as the passage of a comet near the sun. The only difference is that the force in our electrical problem is one of repulsion, while in the case of gravitating bodies the force is attractive. The solution of the problem is contained in standard works on dynamics and presents no difficulties. It is there shown that if p is the distance of the fixed particle, in this case the nucleus of the gold atom, from the original path of the α-particle, the latter will be deflected through an angle ϕ given by the relation

$$p = \frac{E_1 E_2}{2T} \cot \frac{\phi}{2}$$

where E_1, E_2 are the two charges, and T is the kinetic energy of the α-particle, which is known since we know its mass and its velocity. All the particles which pass nearer a gold nucleus than this will be deflected through an angle greater than ϕ.

If we look at our gold leaf in the direction in which the incident beam is travelling and describe small circles of radius p around each gold nucleus the probability that an α-particle will pass nearer the nucleus than p is obviously the probability that its path will intersect one of these circles, and is thus proportional to the sum of the areas of these circles, providing that they are so small that they do not overlap. Thus if n is the number of gold atoms in unit volume and t is the thickness of the leaf the probability that the particle will pass nearer than p to a gold nucleus is equal to the area of one of these circles multiplied by their number, that is to $\pi p^2 . nt$. All these particles will be deflected through an angle greater than ϕ. Hence the fraction ρ of the whole number of α-particles whose paths after passing through the leaf make a greater angle than ϕ with the original direction is given by

$$\rho = \pi nt \left(\frac{E_1 E_2}{2T}\right)^2 \cot^2 \frac{\phi}{2}$$

$$= \pi nt \frac{N^2 e^4}{T^2} \cot^2 \frac{\phi}{2} \quad . \quad . \quad . \quad (11)$$

on the assumptions we have already made as to the charges.

If, now, we take a circular screen, subtending some known angle ϕ at the gold leaf, we can easily determine by counting the scintillations on the screen with and without the leaf, what *fraction of the particles* are deflected off the screen by the leaf. The experimental methods of counting α-particles have been described in an earlier chapter. As we have only been able to calculate the chance of a particle being deflected we must count a sufficiently large number of particles for the laws of probability to apply, but, after a little practice, the experiment is tedious rather than difficult. The formula, which was first given by Sir Ernest Rutherford, has been put to the test, first by Geiger, and recently by Chadwick, and has been shown to represent the scattering of the α-particles to an accuracy of at least 1 per cent. There can be no doubt, therefore, that Rutherford's assumptions are correct, and that the positive charge on the atom is concentrated, as he supposed, on a nucleus of dimensions very much smaller than that of the atom.

We can, however, go further than this. If we measure the angle subtended by the screen at the scattering substance, and the fraction ρ of the particles scattered outside this angle, all the quantities in equation (11) are known with the exception of N, which measures the number of times the charge on the nucleus is greater than the electronic charge. Since the atom as a whole is neutral, N is also the number of electrons in the atom.

Some particularly accurate determinations of the nuclear charge have been made by this method by Chadwick, who worked with thin foils of copper, silver and gold. The values obtained for the nuclear charges on these elements were respectively 29·3, 46·3 and 77·4. Now if we arrange the elements in the order of their ascending atomic weights we find that copper is twenty-ninth on the list, silver forty-seventh and platinum seventy-eighth. Now the nuclear charge must in any case be a whole number, and it is

clearly something more than a coincidence that the whole number representing the nuclear charge should be identical, in the case of these three elements, with their number in the table of ascending atomic weights. We may take it then that the *order of the element in the table of ascending atomic weights, or the atomic number of the element, as it is called, measures also its nuclear charge*. This suggestion had previously been made by van der Broek. It has been conclusively verified by these experiments on the scattering of α-particles.

Experiments of this type can, however, give us still more information as to the nuclear properties. It has been assumed in the previous analysis that the α-particle and the nucleus behave as charged points, repelling each other in accordance with the inverse square law of force. If the particles come into such close collision that their size becomes appreciable in comparison with the distance between them, or, above all, if they come into physical contact, the inverse square law will no longer hold, and the formula (11) will break down. Chadwick verified the formula very carefully in the experiments just described, and found that it held with accuracy. The distance of nearest approach of the particles can be calculated from the magnitude of the deflections produced, and in Chadwick's experiments was of the order of 3×10^{-12} cm. in the case of copper. Up to this point the copper nucleus behaved exactly like a point charge. The radius of the copper nucleus must, therefore, be distinctly smaller than 3×10^{-12} cm. Thus practically the whole mass of the copper atom is concentrated in a particle the diameter of which is not more than one ten-thousandth of that of the atom itself. The remainder of the atom is an empty void save for a few wandering electrons, twenty-nine in the case of copper, sailing through its vast empty spaces like planets round a central sun.

Since the force repelling the particle from the nucleus varies as the charge on the nucleus and thus as its atomic number, we might hope to approach more nearly to this

fundamental particle by working with elements of very low atomic weight, and, in particular, with hydrogen, the lowest of them all. The hydrogen nucleus has, besides, a particular interest of its own. Aston's discovery that the masses of all atoms are integral numbers has thrown us back again on Prout's hypothesis, that in hydrogen we may have the protyle from which all the elements are constructed, or, as we should put it now, that the hydrogen nucleus is the fundamental particle from which all other nuclei are built. It should, therefore, occupy a unique position.

The problem of the hydrogen nucleus was attacked first by Rutherford. The problem of the scattering of α-particles by such a light nucleus as that of hydrogen is more complex than that of the heavier nuclei. The mass of the hydrogen nucleus is only one quarter of that of the α-particle. It will thus be set in motion by the impact, just as one billiard ball is set in motion when cannoned into by another, and both the motions have to be taken into account. This is quite obvious when the hydrogen is in the form of a gas, where the atoms are free to move. It is found, however, by experiment that exactly the same considerations apply when the hydrogen is combined in the solid form, as, for example, in paraffin wax. The forces binding the hydrogen in the molecule of wax are completely negligible in comparison with the terrific forces called into play by the impact of the α-particle. Thus, while Rutherford's early experiments used hydrogen gas as the scattering substance, later experimenters prefer, for reasons of convenience, to work with the hydrogen in the form of wax.

The problem is completely soluble if we assume that the colliding nuclei behave as charged points, and not only can the deflections of the α-particles be calculated, but also the velocity and distribution of the projected hydrogen particles. These velocities are so large that the hydrogen particles cause scintillations when they fall on a fluorescent screen, and their tracks can thus be determined by the methods employed for the α-particle.

On passing a beam of α-particles into *hydrogen gas* Rutherford found that hydrogen atoms were projected directly forward with such high velocities that they produced scintillations on a screen placed far outside the range of the α-particles themselves. The range of the fastest hydrogen particles was, in fact, about four times that of the α-particles employed, which implies that their velocity is at least 1·6 times greater. To produce this velocity it is necessary that the centres of the two particles should have approached within a distance less than 3×10^{-13} cm. The sum of the radii of the two nuclei must, therefore, be less than this, assuming that the inverse square law of force holds down to this minute distance.

If we assumed that the two nuclei were of the same size, each would have a radius rather less than that of an electron. On the other hand, as we shall see later, the helium nucleus is certainly complex and contains probably two electrons. The radius of the hydrogen nucleus must therefore be less than that of the electron; how much less we cannot yet say, since these experiments only fix an *upper* limit to the size of our particles. The probabilities are that the size of the hydrogen nucleus is very much smaller than that of the electron, and Chadwick and Bieler account very satisfactorily for their experimental results on this assumption.

We are thus again brought within reach of the possibility of assigning to all mass an electromagnetic origin, which eluded us in the case of the negative electron. The electromagnetic mass of a charge is inversely proportional to its radius. Now the charge on a hydrogen nucleus is equal to that on an electron, since the atomic number of hydrogen is unity. If we assume that the radius of the hydrogen nucleus is 1/1845 of that of the electron, or approximately 10^{-16} cm., its mass would be 1845 times that of the negative electron; that is to say, its electromagnetic mass would be equal to the mass of the hydrogen atom. Although the proposition cannot be said to have

been proved, the arguments and experiments just described have shown that the hydrogen nucleus is at any rate so much smaller than the electron, that there is no improbability in the assumption, and probably no physicist would reject an hypothesis which is so agreeable to his sense of the fitness of things. The electromagnetic origin of matter may in short be regarded as firmly established.

The hydrogen nucleus, that is to say the atom of hydrogen which has lost its attendant electron, may thus be recognised as the long-sought-for "positive electron," which had in fact eluded its pursuers in the same way as the purloined letter in Poe's well-known romance, merely by its excessive obviousness. Its charge is equal in magnitude but opposite in sign to that of the negative electron, and its mass like that of the negative electron is purely electrical in origin; and is equal to, or rather we should say, *is* the mass of one hydrogen atom, on account of the very much smaller space in which it is concentrated. Sir Ernest Rutherford has proposed to call this particle a "*proton*." The suggestion has not yet met with universal acceptance, but it forms such a convenient alternative for the phrase "positively charged hydrogen nucleus," that we will adopt it in the present volume.

Our ideas of the structure of the atom are now becoming clear. An atom consists of a central nucleus of comparatively small dimensions, in which practically the whole mass of the atom resides. Outside this nucleus, and probably at comparatively large distances from it, are a sufficient number of electrons to make the system as a whole electrically neutral. The number of these electrons is equal to the atomic number of the element. Our many probings of the atom have revealed nothing apart from these two sets of particles. We must, therefore, picture the atom as a sort of void in which a comparatively few, minute, negatively charged planets circulate around a central positively-charged sun. In fact, considered as a

planetary system, the atom is even more open than our own.

The simplest atom, that of hydrogen, consists of a single proton and one attendant electron. Since the two particles are oppositely charged they attract each other, and the most elementary knowledge of electrostatics is sufficient to show that such a system is unstable if the particles are at rest. We can, however, produce a temporary stability by setting the electron rotating about the proton with a high velocity, just as the planets are prevented by their motion from falling into the sun. Now, according to the ordinary laws of electromagnetism, as we know them at present, such motion of the charged particle would necessitate a very considerable emission of electromagnetic waves, and thus produce such a constant drain of energy from the system as would rapidly reduce it to a state of rest. Our only mode of escape from this unpleasant dilemma, so far as we can see at present, is to assume that for reasons at present entirely unknown to us an electron can rotate in certain definite orbits about a positively-charged nucleus without producing any radiation at all. This is the assumption made by Bohr.

Let us leave for the present, however, this question of stability and confine our attention for the moment to the nucleus. The second element, helium, has an atomic number 2, and the charge on its nucleus is, therefore, twice that on the proton. On the other hand, its mass is approximately four times the mass of the proton, or hydrogen nucleus, so that four protons would be required to produce the necessary mass. It might, of course, be assumed that the helium nucleus was a new particle formed by a still greater concentration of the positive electricity, but this is not a solution which would readily appeal to the scientific imagination. The simplest hypothesis is that the helium nucleus consists of four protons, which would give it the necessary mass, together with two negative electrons, which while leaving the mass

practically unaltered, would reduce the effective charge of the particle as a whole to two.

Before leaving the subject of the helium nucleus attention must be drawn to some exceedingly ingenious experiments recently made in the Cavendish Laboratory, by which light has been thrown not only upon the size but also the " shape " of the helium nucleus. In the calculations of the size of the nucleus, which we have already described, it was assumed that the inverse square law of force continued to hold for the very small distances of approach which obtain in these collisions. The matter can, however, be put to the proof. Mechanical theory allows us to calculate both the distribution of velocities among the scattered hydrogen nuclei, and the probable direction in which they will be scattered. It was found that if the experiments were carried out with a beam of comparatively slowly moving α-particles these predictions were fulfilled. If, however, more rapidly moving particles were employed the behaviour of the hydrogen particles was quite different. Instead of being scattered in all directions around the path of the particles, the majority of them were driven straight forward in the direction of the beam. This could only occur if the helium nucleus behaved like a flattened disc travelling face forward. A mechanical analogy will make this clear. If we project a billiard ball into a crowd of ping-pong balls the latter will be scattered in all directions. If, however, we drive at the crowd with a cricket bat, taking care, as we always should, to keep a straight bat, the ping-pong balls will all be projected straight forward in the direction in which the bat is moving. In the case of the collisions between the α-rays and the hydrogen nuclei the actual result is somewhere between the two extreme cases. Chadwick and Bieler calculated that their experimental observations would be satisfactorily explained if the helium nucleus was a flattened spheroid, the major and minor axes of which were about 8×10^{-13} cm. and 4×10^{-13} cm. respectively. It is, of course, highly improbable that this rather crude picture

represents the actual helium nucleus, or α-particle. What is asserted is that outside this spheroid the helium nucleus behaves approximately as a point charge, while within it the repulsive forces increase so rapidly that the hydrogen nuclei are driven forward from it as if by a rigid surface.

It is interesting to recall that the diameter of an electron, as deduced from electromagnetic theory, agrees very closely with this estimate of the thickness of the nuclear spheroid of helium. Since the nucleus consists of two electrons and four protons the results of Chadwick and Bieler may be regarded as furnishing additional and very convincing evidence, firstly, that the radius of an electron as deduced from the electromagnetic theory is a very close approximation to the facts, and, secondly, that the proton is a particle much smaller still.

This new and fascinating sport of atomic billiards is being vigorously pursued under Sir Ernest Rutherford in Cambridge. We shall have occasion later to refer to some events in which the impacts are so violent that the balls get broken in the process. New methods of recording the strokes have also been evolved and are being used with much success, particularly by Blackett. We have seen that the track of an α-particle can be made visible by C. T. R. Wilson's beautiful cloud method. The track of the smitten nucleus can also be made visible in the same way. Thus, if a suitable collision takes place within the gas in an expansion chamber the whole process can be recorded on a photograph, the tracks of the particles being represented by lines, as in some diagram in a text-book on mechanics. By the kindness of Dr. Blackett I am able to reproduce one of his photographs in Fig. 20. The photograph shows two views of the same collision taken in two directions at right angles to each other, so that the actual angles between the various tracks can be calculated, and from them the relative masses of the colliding particles. It will be seen quite clearly that while most of the α-particles cross the field of view without any deflection, as Rutherford's theory demands, one of them actually comes

into oblique collision with an atomic nucleus. The colliding α-particle is deflected from its course by the collision, while the nucleus struck is projected violently across the diagram. Photographs of this kind leave no possible doubt as to the reality of the phenomena which we have been describing.

The strongest evidence in favour of the assumption that the nuclei of the atoms of higher atomic weight are complex is furnished by the discovery, which we have already mentioned, that the actual masses of the different

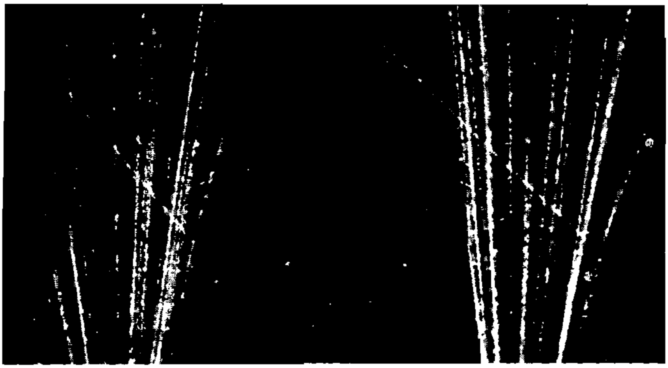

FIG. 20.—Collision of an α-particle with a helium atom.

atoms are all whole numbers to a very considerable degree of accuracy, if the mass of one atom of oxygen is taken as exactly 16. The only possible explanation which can be given of such an effect is that all the atoms are composed of differing numbers of particles whose mass on the same scale is represented by unity. We have, indeed, to allow that the atom of hydrogen, our lightest element, has a mass which is slightly, but certainly, greater than unity on the scale we have selected, but this exception causes no real difficulty. In calculating the electromagnetic mass of a particle we assumed that its field was uniformly distributed about the particle. This will only be the

case if the particle is relatively distant from all other charges. This is true in the case of the nucleus of the hydrogen atom, which consists of a single proton. It is far from true in the case of a helium nucleus where, if our theory is correct, we have four protons and two electrons concentrated in a space which is certainly not much larger than the volume of a single electron. It can be shown that the effect of this exceedingly tight packing of the particles is to reduce the electromagnetic mass. To put the matter very crudely we might almost say that the tubes of force in the nucleus are so closely crowded together that there is hardly enough ether to go round, so that each grips rather less than it would in the absence of the others. In the case of the helium nucleus the loss of mass amounts to $(4 \times 1{\cdot}008) - 4{\cdot}00$, or about ·032 in atomic units.

Since the masses of the atoms of other elements are all whole numbers, if helium is taken as exactly 4, we must assume either that the average closeness of the packing of protons and electrons is the same for all atoms, or that the higher atomic nuclei are composed mainly of helium nuclei, together with the minimum number of protons and electrons to give the proper mass and charge. As we shall see, the latter hypothesis seems to be the one which is supported by experiment. Before passing on, however, it may be interesting to point out a result which follows from this loss of mass on Einstein's Relativity theory. According to this much-discussed theory, mass and energy are interchangeable terms, so that while energy in any form may be said to possess mass, so also mass in any form must be supposed to imply energy. In fact, the energy of a mass m at rest is supposed to be equivalent to mc^2 ergs or units of energy where c is the velocity of light. Suppose that by some means we can convert 1 gram of hydrogen, that is to say, the hydrogen contained in 18 cubic centimetres of water, into helium. There will be a loss of mass amounting to about ·008 gram in the process, owing to the packing effect which we have just considered.

Since the velocity of light is 3×10^{10} cm. per second, this should result in the liberation of an amount of energy equal to $\cdot 008 \times 9 \times 10^{20}$ or about $7{\cdot}2 \times 10^{18}$ ergs. If converted into heat this would give us about $1{\cdot}7 \times 10^{11}$ calories, or if converted into electrical energy it would be sufficient to run a 2,000 kilowatt motor continuously for more than four days.

The element lithium has an atomic number 3, and hence 3 is also the resultant positive charge on the lithium nucleus. Its average or chemical atomic weight is 6·94, but it has been shown to consist of a mixture of two isotopes with atomic masses of 6 and 7 respectively. There is no difficulty in accounting for the existence of isotopes on the nuclear theory we are discussing. In fact it may be regarded as somewhat surprising that the number of isotopes is not greater. Given a sufficient number of protons and electrons there is no limit to the number of systems which could be devised with a resultant charge of 3. There must, however, be some principle, about which we have not at present even sufficient data for speculation, which renders the vast majority of these conceivable systems unstable. The lighter lithium nucleus is obviously made up of six protons and three electrons, while the heavier one, which forms the greater part of the mixture, has a nucleus with seven protons and four electrons.

At any distance which is large compared with the radius of the nucleus each of these lithium nuclei will behave as a point charge of three units. Each will require three additional or external electrons, as we may call them, to produce a neutral atom, and as we have direct evidence that these external electrons are distant from the nucleus by at least 100 times its radius, the arrangement of these electrons in the atom and the forces which bind them in position will be identical in the two cases. In short, the two atoms will be identical in everything except the mass of the central nucleus, and will thus exhibit identical chemical and physical properties, except for the few

phenomena which depend directly on the mass of the atom.

The composition of the nucleus of any given atom can easily be deduced on the principles followed in the case of the two lithium atoms. The number of protons must be equal to the atomic mass of the atom; while the nucleus must also contain sufficient negative electrons to reduce the resultant positive charge on the nucleus to the atomic number.

The fact that the aggregation of four protons to form helium is attended with such an enormous evolution of energy indicates that the helium nucleus is an exceedingly stable structure. It seemed not improbable, therefore, that the nuclei of the heavier elements might be built up mainly of helium nuclei existing within the heavy nucleus as such, rather than of independent protons. Some support was given to this conjecture by the fact that the material particles shot off by a radioactive substance during disintegration invariably consist of helium nuclei. The fact that β-particles are also a product of radioactive disintegration may be regarded as direct evidence for the existence of electrons within the nucleus itself. It would be impossible for an electron to acquire the very high velocities which are exhibited by the β-rays in the comparatively weak electric fields which exist outside the nucleus.

The matter has, fortunately, been placed beyond doubt by some recent experiments by Sir Ernest Rutherford. When the rapidly moving α-particles from radium C were passed through pure nitrogen it was found that occasional scintillations were obtained on a fluorescent screen at distances far greater than could be traversed by the α-particles themselves. The range of these particles suggested that they were atoms of hydrogen, and this suggestion was confirmed by determining their deflection in a magnetic field. We are thus dealing with a genuine disintegration of the nitrogen atom, a real transmutation of elements. One of the products of this transmutation

is, as we might have expected, the proton, or hydrogen nucleus. In addition to these long range particles, however, a considerably larger number of more slowly moving particles were also produced which were finally identified with helium. Thus the disintegration of the nitrogen atom yields helium and hydrogen.

If the experiment is repeated in oxygen, however, no long range hydrogen particles are produced, only the more slowly moving helium atoms. In general, elements whose atomic weight is an exact multiple of 4 yield only helium, those whose atomic weight is not an exact multiple of the mass of a helium atom give helium and hydrogen. Such facts strongly suggest that the helium nucleus as such is the substance from which the heavier nuclei are mainly built up, and it is only the protons in excess of the number which can be arranged into groups of four which exist in a relatively free condition in the nuclei. Since the mass of a free proton is somewhat greater than its mass when combined in a helium nucleus, the mass of the atoms containing free protons should be slightly greater than the nearest whole number. Unfortunately, the accuracy at present attainable in the measurement of the masses of the heavier atoms is not sufficient to enable us to test the matter in this way.

It might be thought that in demonstrating the minuteness of atomic nuclei we had automatically proved the impossibility of determining their intimate structure. The problem is indeed a difficult one, but there are already indications that it is not insoluble. Some of the heaviest nuclei are unstable, and from a study of the radiations which they emit during their dissolution we may hope to obtain information as to their original structure. Already it seems fairly certain that the architect who placed the planets in the heavens, and arranged the electrons in the atom according to a very similar scheme, has used a device of much the same type in this smallest and most fundamental structure of all. But in the nucleus we are approaching very near the heart of the

mystery of matter, and it is possible that progress may be slow.

Fortunately this problem stands apart from the other problems presented by the atom. At all appreciable distances, even within the atom, it behaves like a single point, and all that concerns us is its mass, which is the mass of the atom, and its resultant charge, which fixes the number and the arrangement of the planetary electrons. It is to the latter that we must look for an explanation of the chemical and physical properties of the atom.

The adoption of a nuclear theory of the atom, though it has been forced upon us by evidence of the clearest and most convincing kind, raises fundamental difficulties. As we have seen, any arrangement of electrons around a central point charge is unstable on our classical theories of mechanics and electricity, which must, therefore, be modified in directions which only experiment can point out. The properties of the atoms themselves must guide us, and of these the most important for our purpose are their chemical properties and their spectra. We will consider these separately in the chapters which follow.

CHAPTER VII

THE ELECTRON IN CHEMISTRY

One of the earliest and certainly one of the greatest of the great generalisations of Chemistry is the Periodic law, the fact that, if we arrange the elements in the order of their ascending atomic weights, certain chemical properties tend to *recur* at definite intervals in the scale. Thus we get families or groups of elements bearing very close resemblances to each other, such as the alkali metals, the inert gases, and the alkali earths. These families seem to be linked together in some way, so that a member of the halogen family is always followed immediately in the list by an inert gas, and the inert gas is succeeded by a member of the alkali group. Many attempts have been made to classify the elements on this basis and much ingenuity has been spent in striving to fit the whole of the ninety-two elements into a rigid and symmetrical scheme; so much indeed that some chemists have in their impatience been tempted to abandon the classification altogether. Of the periodicity in the properties of the elements, however, there can be no doubt, though the periodicity is not quite so simple as was at one time imagined. A very usual form of classification is given in the Table on pp. 96, 97.

The very remarkable facts embodied in this table received their first explanation from Sir J. J. Thomson. It is to him that we owe the first suggestion that the properties of the elements were due to the various groupings of electrons inside the atom, and he was the first to discover the main principles of electron grouping, principles which, in the main, hold good for the more recent and more accurate arrangements deduced by Bohr.

Assuming that the positive electricity in the atom occupied a sphere of atomic dimensions, Sir J. J. Thomson showed that a single electron if at rest will place itself at the centre of the sphere, or if in motion will describe a circle about that point. Two electrons would occupy positions at equal distances from the centre of the sphere, while three would arrange themselves at the corners of an equilateral triangle. The arrangement of four electrons at the corners of a square is not a stable grouping, unless the system is rotating with more than a certain critical speed. If the velocity falls below this critical value the system collapses into a regular tetrahedron. Six electrons would occupy the corners of a regular octahedron. The arrangement of eight electrons at the corners of a cube is, however, unstable, and would collapse into two tetrahedra, one inside the other, thus forming two shells of electrons. The cube, however, is a stable grouping if one or more additional electrons are placed within it.

At this stage the mathematics of the problem becomes practically impossible. The problem can be simplified still further by assuming that the electrons instead of being arranged in three dimensions are confined to a single plane. This case has the advantage that it can be studied experimentally in various ways. Of these the very beautiful experiments of Mayer, though designed for quite other purposes, are perhaps the simplest to reproduce.

A large number of needles are magnetised together in a solenoid, and are floated vertically in a basin of water by pushing all their (say) north poles into small corks, their south poles being at the same depth below the water. These latter repel each other, just as do the electrons according to an inverse square law. To represent the action of the positive sphere we may place a strong electro-magnet beneath the bowl with its north pole upwards. It can be shown that the attraction of this magnet for the tiny south poles is (for the horizontal plane in which alone they are able to move) approximately

TABLE VI.—PERIODIC

GROUP O.	GROUP I.	GROUP II.	GROUP III.	GROUP IV.
				1. Hydrogen
2. Helium. 4·00	**3.** Lithium. 6·94 [6, 7]	**4.** Beryllium. 9·1	**5.** Boron. 10·9 [10, 11]	**6.** Carbon. 12·00
10. Neon. 20·2 [20, 22]	**11.** Sodium. 23·0	**12.** Magnesium. 24·3 [24, 25, 26]	**13.** Aluminium. 27·1	**14.** Silicon. 28·3 [28, 29, 30]
18. Argon 39·9 [36, 40]	**19.** Potassium. 39·1 [39, 41]	**20.** Calcium. 40·07 [40, 44]	**21.** Scandium. 45·1	**22.** Titanium. 48·1
	29. Copper. 63·57 [63, 65]	**30.** Zinc. 65·37 [64–70]	**31.** Gallium. 70·1 [69, 71]	**32.** Germanium. 72·5 [70, 72, 74]
36. Kypton. 82·92 [78, 80, 82, 84, 83, 86]	**37.** Rubidium. 84·45 [85, 87]	**38.** Strontium. 87·83 [86, 88]	**39.** Yttrium. 89·33	**40.** Zirconium. 90·6 [90, 92, 94]
	47. Silver. 107·88 [107, 109]	**48.** Cadmium. 112·40 [110–116]	**49.** Indium. 114·8	**50.** Tin. 118·7 [106–122]
54. Xenon. 130·4 [128–136]	**55.** Caesium. 132·81	**56.** Barium. 137·37 [136, 138]	**57** to **71.** Rare earths. Atomic weights between 139 and 178.	**72.** Hafnium. 178·6
	79. Gold. 197·2	**80.** Mercury. 200·6 [199–204]	**81.** Thallium. 204·0	**82.** Lead. 207·2 [206–214]
86. Radon. [218, 220, 222]	**87.** — —	**88.** Radium. 226·0	**89.** Actinium —	**90.** Thorium. 232·15

The atomic numbers of the elements are given in bold type; the atomic weights in ordi-
determined are enclosed in square brackets. The atomic number of uranium has been shown
squares in the last two series are occupied by more than one radioactive substance. Only
within the dotted lines are those which, according to Bohr's theory, have two unsaturated
ness to the normal elements in their own groups.

CLASSIFICATION OF THE ELEMENTS

GROUP V.	GROUP VI.	GROUP VII.	GROUP VIII.		
7. Nitrogen. 14·00	**8.** Oxygen. 16·00	**9.** Fluorine. 19·00			
15. Phosphorus. 31·0	**16.** Sulphur. 32·0	**17.** Chlorine. 35·5 [35, 37]			
23. Vanadium. 51·0	**24.** Chromium. 52·0	**25.** Manganese. 54·94	**26.** Iron. 55·85 [54, 56]	**27.** Cobalt. 58·97	**28.** Nickel. 58·7 [58, 60]
33. Arsenic. 74·96 [75,]	**34.** Selenium. 79·2 [74–80]	**35.** Bromine. 79·92 [79, 81]			
41. Niobium. 93·5	**42.** Molybdenum. 96·0	**43.** Masurium. —	**44.** Ruthenium 101·7	**45.** Rhodium. 102·9	**46.** Palladium. 106·7
51. Antimony. 120·2 [121, 123]	**52.** Tellurium. 127·5 [126, 128, 130]	**53.** Iodine. 126·92 [127]			
73. Tantalum. 181·5	**74.** Tungsten. 184·0	**75.** *Rhenium.* —	**76.** Osmium. 190·9	**77.** Iridium. 193·1	**78.** Platinum. 195·2
83. Bismuth. 209·0	**84.** Polonium. —	**85.** — —			
91. *Protoactinium.* —	**92.** *Uranium.* [234, 238]				

nary type below the name of the element. The masses of isotopes where they have been
to be 92 by direct experiment. This leaves two vacant squares in the table. Several of the
the most stable of these are shown, to avoid overcrowding the table. The elements included
outer rings. This explains the resemblance of these elements to each other and their unlike-

proportional to their distance from a point immediately above the pole. Fig. 21 is a photograph showing ten of these small magnets. It will be seen that they are arranged in two rings of seven and three respectively. The attracting electro-magnet is concealed below the board.

On making the experiment it is found that the greatest

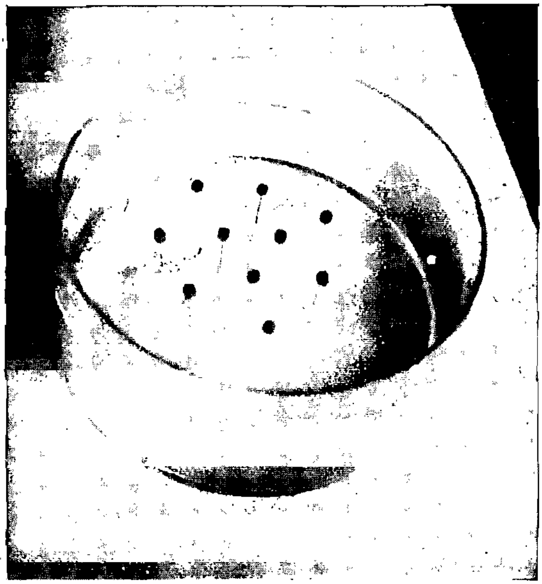

FIG. 21.—A "model" atom.

number of magnets which we can have in an empty ring is five. If a sixth is added the ring breaks up, the magnets gradually settling down into an arrangement of five on the outside with one in the middle. The number which must be placed in the middle rapidly increases with the number in the outer ring. Sir J. J. Thomson calculated that an outer ring of twelve electrons required at least eight inside, and one of thirty no less than 101 for stability

to be possible. As these inner electrons are subject to exactly the same laws as the outer ones, the whole system splits up into a series of concentric rings, with a perfectly definite number of particles in each.

These results bring out, quite clearly, what we may call the principles of electron grouping. Just as in the three-dimensional solution it was found that the electrons arranged themselves in concentric shells, so in the two-dimensional plane the electrons arrange themselves in concentric circles. Further, a shell or circle containing a definite number of electrons is unstable unless there are at least a certain minimum number of electrons within it. We are thus brought face to face with one of the most important generalisations in the problem of electron grouping, namely, that it is impossible for any system to have a large number of electrons near its surface without a corresponding number within. To use a commercial metaphor, an atom cannot put all its goods in the shop window. There must be a correspondingly large stock inside or otherwise there will be an inevitable collapse into some less pretentious system. These two principles, which, it may be said, are amply supported by Bohr's more recent calculations, will be found to lead us far in the practical solution of our problem.

This tendency in the electrons to form stable groups has, as an immediate consequence, that the electrons are not all held in the atom in the same way, or with the same binding force. The electrons, over and above the number which can be combined into these stable aggregations will be at once more free to move about in the atom, and less strongly attached to it. They will, in fact be very largely screened from the attraction of the central nucleus by the intervening groups of electrons which separate them from it, and their removal from the atom may be effected comparatively easily. We know now that it is possible to detach an electron even from the innermost groups of the atom without interfering seriously with its internal economy; the missing electron being

immediately replaced by another from the outer part of the structure. The forces required are, however, much greater than those required to detach an electron from an incomplete group, and we may regard the latter as comparatively free. The existence of such comparatively free electrons is not a mere theoretical postulate or deduction. It is required by phenomena as diverse as the ionisation of gases, the conductivity of metals, and the dispersion of light. Experiments on optical dispersion have shown that the number of these comparatively mobile electrons in a given quantity of matter is not many times greater than the number of atoms present, and that they thus form only a fraction of the whole number of atomic electrons; similar results are obtained from a consideration of the number of free electrons in a metallic conductor. We shall see later that these mobile electrons determine the chemical properties of the atom. They are therefore usually spoken of as *valency* electrons, or occasionally, from their action on light, as the *dispersional* electrons.

Let us suppose, to put the matter in perfectly general terms, that we have an atom containing A electrons, which have arranged themselves in stable shells or orbits, together with N additional electrons, so that the atomic number of our element is A + N. We will suppose further that the A electrons would be just sufficient to stabilise an outer ring of B electrons, where B is some number greater than N. We could, as we have seen, extract by suitable means the N valency electrons, leaving the atom with A electrons in their stable grouping, and a central positive charge of A + N. But as we have seen the A electrons form a stable group even when the central charge is only equal to A. It would, therefore, be much more stable if the attractive charge on the nucleus is increased to A + N. We should not expect to be able to withdraw any further electrons from the atom, except by forces sufficiently great to disrupt the whole atomic structure. The withdrawal of the N electrons would leave the atom, as

a whole, with a resultant positive charge of N in electronic units.

Instead of losing, however, the atom might absorb electrons. Suppose it to absorb sufficient to allow of the formation of an outer shell of B electrons. This system is just stable when the nuclear charge is A + B, that is equal to the total number of electrons in the atom. As however, the nuclear charge on our atom is less than this (since N is less than B), the new arrangement would be on the verge of instability, and obviously could not hold any further electrons, without an increase in its nuclear charge, which would mean the creation of an entirely different atom.

The two numbers A and B thus constitute, as it were, barriers which we cannot pass. We may extract N electrons from the system, leaving the atom with a positive charge of N, or we may add to it B − N electrons, giving it a negative charge of B − N. More than this we cannot achieve. The sum of these two quantities is the same for all elements having atomic numbers between A and B, and is equal to the number of electrons B in the complete outer shell. This is an important point to which we shall return.

If, now, we can identify the particular elements in which all the electrons are combined into stable groupings, their atomic numbers will give us the number of electrons in each successive ring or shell, and we shall thus be able to determine from purely chemical considerations the actual arrangement of the electrons in the atoms of the different elements. This is the method adopted by Langmuir. The method is, of course, entirely empirical. It enables us to determine, with some certainty, what the arrangement must be ; it does not show us, from first principles, why the arrangement must be so. But life is short, while art is long, particularly that of the mathematical physicist, and it is perhaps unreasonable to expect the chemist to wait for a hypothesis until the mathematicians have extricated us from those fundamental difficulties of atom building, to which we have already alluded.

It is obvious that an atom in which all the electrons were combined into stable systems would present very marked and peculiar characteristics. In the first place, since it contains no free or dispersional electrons its optical dispersion would be very small, while for the same reason it would possess no electrical conductivity. Again, since all the electrons are combined into closed rings it would exert practically no electric force outside its own radius, and would therefore exert little or no attraction on surrounding atoms. Thus it would form no chemical compounds, not even combining with other atoms of its own kind to form molecules, and for the same reason all the inter-molecular forces which bind together the molecules of solids and liquids, would be so small that we might safely prophesy that it would be a gas of very low boiling point. All these properties are exhibited by the elements helium, neon, argon, etc., which form the group of inert gases. We may therefore say with some certainty that the elements constituting this group are those in which all the electrons are fixed.

Since the atomic number of helium is 2, the innermost ring or shell will contain two electrons. Neon, the next member of the inert gases, has an atomic number, 10, and presumably contains two rings of electrons, an inner one of two, like helium, with an outer ring of eight. Another outer ring of eight electrons added to the neon structure will form the ring system of argon (atomic number, 18), which will thus leave the structure 2, 8, 8. Krypton, however, has an atomic number of 36, and hence contains thirty-six electrons. Subtracting the eighteen contained in the three rings of argon we obtain eighteen as the number of electrons in the fourth atomic ring. Continuing in this way we find that the number of electrons in the different complete rings or shells of electrons is, numbering successively from the innermost outwards 2, 8, 8, 18, 18, 32 respectively.

According to Langmuir's theory the electrons in each layer are uniformly distributed on the surface of a spherical

shell or sheath. The eight electrons in the second and third layers for example, might be regarded as being at the corners of a cube. Langmuir also regards them as being at rest in the atom. Neither of these assumptions is an essential part of the theory, and probably neither of them are true.

Elements which immediately succeed an inert gas in the atomic table differ from them by having one additional electron. This electron cannot be built into the group system; it forms, in fact, the first brick in the next group which is about to be built up. Its attachment to the atom is comparatively feeble, and it will readily be expelled from it by fairly weak forces, leaving the atom with a resultant unit positive charge. The atom will thus be electropositive in character, and a good conductor of electricity. It will have, in fact, the characters of the alkali metals. The succeeding element will have two electrons both of which are removable from the atomic structure. They will, however, be rather more firmly attached than the single electron of the preceding alkali metal, so that these elements are also electropositive and metallic, but less electropositive than the preceding alkali metals. We can recognise in them the alkali earths.

If on the other hand we take an element which immediately precedes an inert gas in the atomic table it will lack one and only one electron for the completion of its group system. It may under special circumstances lose the whole of the incomplete group of electrons, but as this would leave the atom with a very strong positive charge, it is not likely to happen very frequently. It is obviously much more likely that it will attract the one further electron which it needs to build up its outermost group, this extra electron giving the atom as a whole a single negative charge. We should expect this element to be strongly electro-negative in character. It forms, in point of fact, a member of the halogen group.

Sir J. J. Thomson's analysis thus furnishes us with a

very convincing explanation of what is the most strongly-marked feature of the periodic classification, the regular and invariable succession, halogen, inert gas, alkali metal, alkali earth. The explanation lies in the fact that each halogen has *one* electron less than the number required to make up the nearest stable grouping, represented by the succeeding rare gas, each alkali metal one electron in

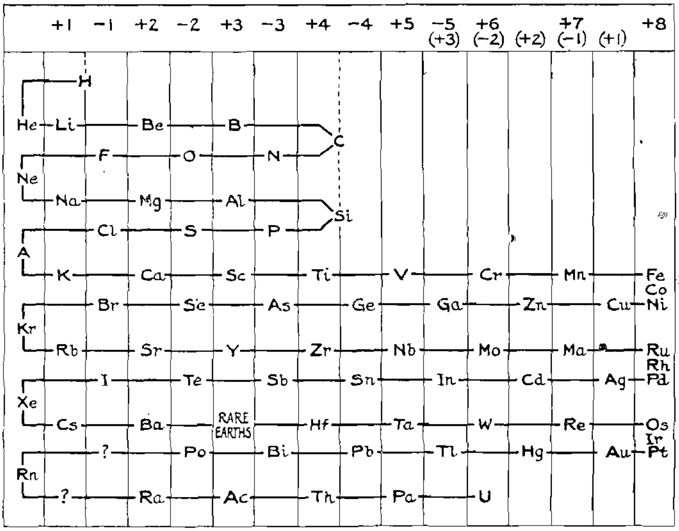

FIG. 22.—The Periodic Table.

excess, and so on. The properties of the elements are thus fixed by their relation to the nearest member of the inert gas family, and it is the recurrence of these stable structures at definite points in the atomic table which gives it its quasi-periodic character.

This is extremely well brought out in an arrangement due originally to Rydberg, and reproduced in Fig. 22. By taking the rare gases as the turning points of the series, we find that all the elements fall into their

most natural groupings. The numbers at the head of the table give the number by which the electrons in the atoms of the elements in the corresponding column exceeds (+) or falls short of (−) the number in the nearest inert gas. It will be seen how accurately this simple criterion sorts the elements into their appropriate classes. Chemical properties are thus largely determined by the completeness or incompleteness of the outer group of electrons.

The case of the elements on the right of the table calls for some comment. The elements in the last column stand by themselves, and it is possible to find some points of resemblance, say, between copper and silver and the alkalis, and between zinc and cadmium and the alkali earths, though these analogies have been sometimes rather overstrained by some chemists in times past. The reason for these anomalies has been made clear by the later work of Bohr which we shall revert to in a later chapter. It appears that the electrons in the atoms of the elements in the last column form groupings which are very nearly complete systems. We may say that these elements have very narrowly escaped being inert gases. Thus the elements in their immediate neighbourhood tend to revert to them, rather than to the more distant inert gases, and the really important fact about the zinc atom, for example, is that it has two electrons surplus to the nickel atom, rather than that it has six electrons fewer than the atom of Krypton. This is indicated by the numbers in brackets at the head of Fig. 22. These facts will become clearer when we are dealing with Bohr's method of grouping the electrons. In the meantime we may say, returning to the more usual form of classification given on pp. 96, 97, the number of comparatively free electrons increases uniformly from one to seven as we pass from Group I. to Group VII. in the table.

Direct experimental confirmation of these results is afforded by experiments on the dispersion of light. We have already mentioned that the dispersion of light is

TABLE VII.—NUMBER OF FREE ELECTRONS IN THE GROUP DEDUCED FROM THE DISPERSION OF LIGHT

Substance.	Calculated number of dispersional electrons.	Number deduced on theory of grouping.
Hydrogen	1·4	1
Calcium	1·5	2
Carbon	3·7	4
Silicon	3·9	4
Oxygen	4·4	6
Chlorine	6·2	7

due to these mobile or valency electrons, and by some rather abstruse and approximate calculations Drude has succeeded in deducing entirely from optical considerations the number of these electrons contained in the atoms of some of the different elements. His results are contained in Table VII. Remembering that the number of electrons must in any case be a whole number, and that the calculations are somewhat approximate in nature, his calculated values would seem to bear out fully the results to which we have been led by our theory of atomic structure.

We are now in a position to deal with what is, perhaps, the most important property of the atom, namely, its power of combining with other atoms to form stable molecules. Of chemical affinity, that elusive and mysterious force, our theory of atomic structure must give some adequate explanation, as, after all, there is no property of an element more characteristic than its power to form compounds with other elements. Ever since the time of Berzelius the view has been held, more or less tenaciously, that the forces binding together the different atoms within the molecule were electrical in their origin; that, for example, the molecule Na.Cl. of sodium chloride was formed by the mutual attraction of a positively charged sodium atom for a negatively charged atom of chlorine. This view was, of course, based on the phenomena of

electrolysis. When an electric current is passed through a solution of sodium chloride in water it is found that the sodium makes its way to the negative electrode, the chlorine to the positive. The salt thus behaves as if the sodium atoms bore a positive and the chlorine a negative charge. It is an obvious assumption that the atoms in the molecule of sodium chloride bear the same charges as they are actually found to possess when in an aqueous solution, and that the electrical attraction between these equal and opposite charges is the bond which unites the two atoms together in the compound molecule.

In the case we have been considering both the elements are monovalent, and it can be shown from the laws of electrolysis that they carry equal and opposite charges. From a consideration of the electrolysis of such compounds as magnesium chloride, $Mg. Cl_2$, in which a divalent atom is combined with two monovalent atoms, it is easy to show that the charge on a divalent atom is twice that carried by the atom of a monovalent element, and that in general there is a direct proportionality between the ionic charge and the chemical valency. This result is a logical and necessary result of the laws of electrolysis.

So long, however, as the ionic charge was regarded as something apart and distinct from the atom itself, something of a different nature superadded to it by mysterious external agency, the electrical theory—except in so far as it explained the phenomena of electrolysis in which it had its rise—was no more fundamental and distinctly less workable than the chemical theory of bonds of affinity. As we shall see later, it is possible to assign a real physical significance to the idea of a bond of affinity.

With the electron theory of matter the situation is quite changed. The electric charge is no mere addendum to the atom. It is a vital part of its structure, and the question whether a given atom will tend to lose or gain electrons, and, if so, how many, will depend entirely on the number and arrangement of the electrons within it and the forces with which they are retained.

To return to the case of sodium and chlorine. We saw at the end of the previous chapter that sodium contains a single mobile or valency electron as we have called it, with which it will readily part under the action of external forces. Chlorine, as we observed, had seven such, but owing to the fact that this number is very close to that required to form a stable ring system, we deduced that chlorine would in general be much more likely to absorb the one electron necessary to achieve this result, and would thus tend to acquire a single negative charge.

Thus, when sodium and chlorine are brought together—the former with a strong tendency to lose an electron, the latter with an equally strong tendency to gain one—it is evident that the mobile electron will pass from the sodium atom to the chlorine, leaving the former with a unit positive charge, and giving the latter a unit negative charge. It may be noted in passing that we have shown in an earlier chapter that the charge carried by a monovalent ion in electrolysis is exactly equal to the charge on an electron. The attraction between these two charges will then be the force which binds the two together in chemical union. As the sodium has now lost its only free electron, while the chlorine atom has acquired the one needed to complete a stable ring system, it is obvious from what we have said of the principles of electron grouping that no further action can take place. The compound is completely saturated.

To come now to the case of magnesium chloride. Magnesium, having, as we have seen, one more electron than sodium, has two mobile, or valency electrons as we have called them, which it can give up under suitable circumstances. But a single chlorine atom can only absorb one. Hence two chlorine atoms are required to denude the atom of magnesium of its stock of mobile electrons, and the compound molecule will consist of one atom of magnesium and two of chlorine, the magnesium having two unit positive charges, and each of the chlorine atoms a single negative charge; in other words, the

magnesium atom is electro-positive *and divalent*. Similarly aluminium with three valency electrons will be trivalent, and so on. *The positive valency of an element* is therefore equal to the number of valency electrons which it contains.

Now we have seen that the number of valency electrons is fixed *by the position of the element in* the Periodic classification, the number increasing uniformly from one in Group I. *to seven in Group* VII. Thus we should expect that the positive valency of the elements would increase *uniformly from one in* Group I. to seven in Group VII. This is found to be the case, though owing *to their extremely electro-negative* character the positive valencies of the elements in the latter group are very *infrequently exerted*.

To pass now to the negative valencies, we have already *seen that the negative valency is determined* by the number of electrons which the atom can absorb. In the case of chlorine this is unity, and chlorine is thus a monovalent electro-negative element. Sulphur, immediately preceding it *in the* table and therefore containing one electron fewer, will require, and can absorb, two electrons to make up a stable ring. It will therefore have a negative valency of two; in other words, the negative valency of the elements will increase from unity to seven as we pass backwards along a series from Group VII. to Group I.

Each element, therefore, on our scheme of atomic structure will possess two valencies—the one positive and equal to the number of valency electrons which it contains,

TABLE VIII.—TABLE OF VALENCIES OF THE PERIODIC GROUPS

Group.	I.	II.	III.	IV.	V.	VI.	VII.
Normal valency .	+ 1	+ 2	+ 3	± 4	− 3	− 2	− 1
Additional or contra-valency .	− 7	− 6	− 5		+ 5	+ 6	+ 7

and the other negative and equal to the number of electrons which it requires to make up, together with those which it already possesses—a fixed electronic system. Thus, phosphorus with five valency electrons would have a positive valency of five, as, for example, in the compound $P.Cl_5$, or a negative valency of three, as in the case of $P.H_3$. Which of these valencies will be exerted will depend largely on the nature of the atom with which it is brought in contact. In general, however, we should expect that the forces acting would tend to make the number of electrons in the atom equal to that stable number to which it was nearest to begin with. Thus elements possessing fewer than four valency electrons would be electro-positive, those with more than four electro-negative; the elements of Group IV. with four valency electrons being indifferently positive or negative. Our complete theoretical scheme of valency is thus represented by Table VIII., where the Roman numerals indicate the group in the Periodic classification. It is most interesting to note that Professor Abegg in an illuminating paper on valency arrived at a precisely similar scheme from a careful study of the chemical compounds of the elements. He suggested that every element had two valencies—a normal and a contra-valency—the normal being supposed to be the stronger. The positive valencies were normal for elements of Groups I. to III., the negative for Groups V. to VII., Group IV. being indifferently positive or negative. In every case the sum of the two valencies was found to be eight. It will be seen that these observations of Professor Abegg are exactly embodied in our theoretical table.

The phenomena of unsaturated compounds present no difficulties. It is not necessary, or indeed to be expected, that the whole of the available electrons should be extracted from the atom in a single stage. It is evident that the work done in extracting the second electron will be greater than that for the first, and it is easy to imagine cases in which the attraction of the combining atom might be

sufficient to produce the withdrawal of one but not of two electrons. Since, however, the atom of higher valency would still contain some displaceable electrons, it would still exert an appreciable force on atoms in its neighbourhood, which, under suitable circumstances, would lead to the addition of further atoms to the molecule. The compound would thus be unsaturated.

The theory of valency, which we have now described at some length, gives such a successful and adequate explanation of the chief facts of valency that there can be no doubt that in the main we have been proceeding along right lines, and that in many cases we have arrived at a very close approximation to the facts. The interchange of an electron between, say, the atom of sodium and that of chlorine in the case of sodium chloride is proved by the charges which these atoms are found to bear when the compound is dissolved. The resultant electrical attraction between the charged atoms is an adequate explanation of the bond of affinity which links them together to form a compound molecule of salt. In other cases, however, the theory, in its simple form presents obvious difficulties. Take as a very simple instance the molecule H_2 of hydrogen gas. The system, consisting as it does of two hydrogen atoms, is a very stable one, requiring a very high temperature for its dissociation. The bond between the two atoms in the molecule of hydrogen is stronger than that between the atoms in the molecules of many compounds. It is impossible to suppose that the bond in this case is radically different from that between the atoms, say, in a molecule of carbon monoxide. On the other hand, since the two hydrogen atoms are exactly similar, it is equally impossible to suppose that there can be any tendency for an electron to pass from one to the other.

Light has again been thrown upon the subject by the researches of Sir J. J. Thomson. His work on the positive particles in the discharge tube, which we have described in a previous chapter, has led him to recognise the existence of two great classes of molecules, namely those in which

the individual atoms are charged as we have assumed on the previous theory, and a second class in which the individual atoms are uncharged. If we suppose, for example, that the atoms in the molecule of carbon monoxide are charged, the carbon positively and the oxygen negatively, we should expect that when the compound was broken down by the stresses in the tube they would retain these charges, just as in the case of an electrolyte in solution to which we have already referred. We should expect, therefore, that there would be an excess of negatively charged oxygen atoms and an excess of positively charged carbon atoms in the resulting stream of particles. As a matter of fact this is not the case. We must conclude, therefore, that the atom leaves the molecule in an uncharged condition, and is thus presumably uncharged when in the molecule itself. On the other hand, the evidence of the positive ray tube is equally clear that in some cases, such as that of water vapour or ammonia gas, the individual atoms do carry a charge away with them when the partnership is dissolved, and are therefore presumably in a charged state in the molecule.

We are thus led to divide chemical compounds into two great classes: those in which the forces between the atoms have not been sufficient to bring about the passage of an electron from the one to the other, and those in which such an exchange has taken place. Molecules of the second class may conveniently be termed "*ionised*," and the process may be spoken of as *intra-molecular ionisation.* In the former class we should naturally place molecules such as H_2, O_2, CO, NO, etc., the constituent atoms of which do not differ very widely in their electro-chemical character; to the second or ionised class we should assign compounds of the more violently opposed elements, such as H_2O, H.Cl, NH_3, together with the whole class of electrolytes. These results are borne out by the experiments with the discharge tube.

We should also expect to be able to differentiate between the two classes of compounds by their physical properties.

It may be pointed out here that although a system may be electrically neutral as a whole, that is to say it may contain equal amounts of positive and negative electricity, it will still be capable of exerting an electrical force in its neighbourhood if the charges are separated by a finite distance. To take the simplest case, the hydrogen atom forms what is known as an electric doublet, and the electrical field around an electric doublet follows exactly the same laws as the magnetic field around an ordinary bar magnet, since the law of force is the same for magnetic poles as for electric charges. The force exerted by the doublet thus depends not only on the magnitude of the charges but also on the distance between them, and is proportional to the product of the two (a quantity corresponding exactly to the magnetic moment of a magnet). In the case of the atom it is this residual field which gives rise to the phenomena of cohesion, rigidity, surface tension, and so on. Now it is evident that the distance between the charges will be greater when the poles of the doublet are situated on different atoms than when both the charges are confined within the same atom. The electrical field will therefore be abnormally large in molecules which are ionised, and the physical characters which depend on this field will be especially well developed. Compounds in which this intra-molecular ionisation occurs should thus be characterised by high surface tension and large latent heats, if liquid, and by great tenacity and rigidity if solid.

A still more valuable criterion is furnished by the specific inductive capacity of the compound. Electrically speaking, we may regard the positive charges on the nucleus and its surrounding electrons as forming a set of electrical doublets. Now, if an electric potential difference is applied to the substance, the electrical doublets will tend to set themselves in such a way that their fields will be opposed to, and will thus tend to diminish the applied field, in exactly the same way that a number of small magnets set themselves in a magnetic field. The result

of this will be that the strength of the field produced by a given electric charge will be appreciably less than it would have been in the absence of any material substance. This phenomenon is known as specific electric induction. Now the greater the strength of these doublets the greater the effect, and hence the greater the specific inductive capacity. Thus compounds in which the charges are attached to separate atoms will be characterised by a high specific inductive capacity.

Again, before the external potential difference is applied, the doublets will be arranged indifferently with their axes in every direction. They are turned into line by the action of the external field itself. Now there will be a great difference in the time taken by the two kinds of compounds to adjust themselves to the external field. The valency electrons, as we have seen, are very light and very mobile. We know from optical phenomena that their natural frequency is comparable with that of ultra-violet light. They will therefore have no difficulty in adjusting themselves to variations in the external field even when they are as rapid as those which occur in the light waves of the visible spectrum.

On the other hand, if the two charges of the doublet are situated on different atoms, the setting of the doublet will necessitate the rotation of the whole massive molecule—obviously a much slower process. Now in the case of ordinary electrical experiments, where the field is usually applied to the substance in the same direction for at least an appreciable fraction of a second, there will be ample time for these heavy doublets to adjust themselves to the field, and they will thus add their full value to the specific inductive capacity of the substance. In the case of such very rapid oscillations of the field as are known to occur in waves of light this adjustment will obviously be impossible, and the specific inductive capacity as deduced from optical experiments will be much less than that obtained from electrical experiments of the usual kind.

Now, Maxwell has shown that on the electro-magnetic

theory of light there is a simple relation between K, the specific inductive capacity of a substance, and n, its refractive index, which may be expressed by the equation $K = n^2$. It is well known that in many cases the value of K deduced from this expression is identical with that obtained by direct electrical measurement, but that in others the relation does not hold even approximately. For example in the case of water, electrical measurements of the specific inductive capacity give a value of about 79, while that deduced from its refractive index by Maxwell's law is only 1·78. This discrepancy between experiment and theory has always been felt to be distinctly unsatisfactory, and science is indebted to Sir J. J. Thomson for this simple, adequate, and elegant explanation. It is an interesting confirmation of the theory that these discrepancies are always to be found in the case of compounds in which we know from independent evidence that the atoms are charged.

We may therefore use the law of Maxwell as a means of determining to which of our two great classes of compounds any given substance belongs. If Maxwell's law holds, as in the case of hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, and nitrous oxide, to mention only a few, the atoms in the molecule are uncharged. If, on the other hand, Maxwell's law does not hold, as is the case for water, the alcohols, ammonia, hydrochloric acid, etc., the compounds belong to the second class, and have intramolecular ionisation. It is obvious that the recognition of these facts will have important bearings in many directions. At present, however, we are only concerned with their application to the subject of valency and the nature of chemical affinity.

We have already seen that an atom, being a system of negative and positive charges, will exert an electric field which extends for some appreciable distance beyond the boundaries of the atom, these forces giving rise to the phenomena of cohesion, rigidity, surface tension, and so on. Now consider a molecule made up of two atoms.

The atoms will attract each other, on account of these electrical forces; they will also be attracted by other atoms and molecules in their neighbourhood. If their attraction for each other is greater than the attraction of the surrounding atoms and molecules, it is evident that they will remain attached to each other, that is to say the molecule will be stable. If, however, the attraction of the external atoms and molecules is comparable with the mutual attraction between the two atoms their union will be dissolved and the molecule will be unstable. From this point of view chemical affinity differs from cohesion and the other molecular forces not in kind but merely in intensity. We may say, then, that from an electrical standpoint a given molecule will be stable if its component atoms do not exert on neighbouring atoms of molecules attractions comparable with those between the individual atoms in the molecule itself. We have now to consider how this condition can be satisfied.

Let us return to the case of a simple doublet, such as we have supposed the hydrogen atom to be. Since one pole is positive and the other negative, the forces exerted at the two ends of the axis will be opposite in character. The immediate force exerted by one atom upon another will thus depend on the orientation of the two when brought together, just as one magnet will either attract or repel another according as we bring opposite or similar poles into contact. As the atoms will come into contact in all sorts of ways the force will on the average be as often repulsive as attractive. If, however, the systems are free to move, they will, by the ordinary laws of mechanics, always arrange themselves so as to attract each other, but this will require a time, the length of which will depend on the rapidity with which the doublets can move. Now the valency electrons are characterised by their great mobility, and will thus adjust themselves very rapidly to fresh conditions. In the case of the fixed electrons in the ring systems the adjustment will require the rotation of the comparatively heavy atomic system. This would neces-

sitate a greater force and a more prolonged connection between the two atoms for its completion. It is therefore unlikely to occur, as the atoms, even in the solid state, are in comparatively rapid motion.

It follows, therefore, that an atom in which all the electrons are fixed will in general be unable to exert any great force on the atoms around it. From an electrical point of view, therefore, a molecule made up of such atoms would be stable, or, in chemical terms, it would be saturated. Our new criterion of saturation is, therefore, simply this, that all the electrons in the atom shall be held fixed by the forces acting upon them. Since only the valency electrons are free to move, the number of electrons requiring to be fixed to ensure saturation is obviously equal to the number of valency electrons which the atom contains.

It remains to be seen now how the electrons can be fixed. It is evident, in the first place, that this can be effected by the passage of the requisite number of electrons from the one atom to the other. Thus, when an electron passes from the atom of sodium to that of chlorine, the sodium atom is left without any mobile electrons, while the addition of the single electron to the seven already present in the chlorine atom fixes them automatically by enabling them to form a stable system. Thus, in the case of molecules possessing intra-molecular ionisation, the valency conditions which satisfy the earlier theory will also automatically satisfy the conditions of the new. For such compounds, therefore, no fresh discussion is required. The case of the molecules in which the individual atoms are uncharged, however, requires further consideration.

It has been suggested by Sir J. J. Thomson that an electron might become fixed by transferring its attraction from its own nucleus to that of some other atom in the molecule. If we regard the electrical action as taking place along a Faraday tube of force it is easy to see that, so long as this tube of force connects the valency electron

with the nucleus of its own atom, it will leave the electron free to rotate within the atom. If, however, the Faraday tube runs from the valency electron to the nucleus of another atom the electron will be anchored, so to say, to the other atom, and will be unable to move without moving one or other of the two atoms. On the other hand, since each atom is neutral as a whole in the class of compounds we are considering, one of the electrons from the second atom must transfer its attraction to the nucleus of the first to neutralise the positive charge which will have been set free. The bond between the atoms is thus a double one, consisting of one inwardly and one outwardly directed tube of force. To take a concrete case, two atoms of hydrogen will attract each other because each contains a mobile electron, and the two systems will therefore be able to adjust themselves so as to make the force between them one of attraction. If, however, the free electron in each atom transfers its tube of force to the nucleus of the other, both will be rendered immobile, and the molecule will be saturated. The union can be represented by the symbol **H$\rightleftarrows$H**, where the arrows indicate the direction of the tubes of force. It will be seen that this connection is perfectly symmetrical, the two atoms functioning, as we should expect, in exactly the same way. The theory thus accounts for the undoubted fact that precisely similar atoms do exhibit for each other a very marked chemical attraction.

The theory, though ingenious, is hardly tenable in its present form. If we consider, for example, the chlorine molecule Cl_2 in which each atom has seven valency electrons, we shall see that the theory requires that each of the fourteen electrons shall transfer its allegiance to the opposite nucleus, and that the two atoms shall be linked together by no less than fourteen tubes of force ; a more than Ethiopian bondage to which it is difficult to subscribe. Again, there seems to be no necessity that the tubes of force which enter and leave a given atom should connect it to the same atom. Thus any number of positive

monovalent atoms of any kind might unite to form a single molecule by linking themselves together in the form of a closed ring. This deduction is not necessarily unfavourable to the theory. There is undoubtedly a tendency on the part of many elements to form molecules, which, especially in the solid state, contain a considerable number of atoms, and it is not impossible that these complex molecules may have the ring structure which Sir J. J. Thomson suggests. Among compounds, however, except in the case of carbon, such an arrangement is very rare, and the theory would certainly require some restriction at this point.

The real difficulty, however, arises when we come to consider the question of negative valency. So far we have been discussing only the valency which arises from the existence in the atom of mobile or valency electrons—that is to say, the positive valency of the atom. It is, however, a perfectly well-established fact that an atom like that of chlorine, which contains a large number of valency electrons, behaves in its most characteristic reactions as a monovalent negative element.

In the majority of cases in which the negative valency is exercised—for example, in the case of the metallic chlorides—the compound possesses intra-molecular ionisation, and is formed with the interchange of an electron. In this case, as we have already pointed out, the new and the older theories become identical, and no difficulty arises. Negative valencies are, however, undoubtedly exercised in compounds such as $C.Cl_4$, which show no signs of intra-molecular ionisation. The passage of an electron is therefore not essential to the existence of negative valency.

To obviate these difficulties, Langmuir suggests that pairs of electrons may be regarded as belonging simultaneously to both of the combining atoms, and that an atom may complete its outer sheath of electrons by using an electron which is already performing a similar function in another atom without at all impairing its efficiency.

Thus, if we regard the seven valency electrons in the chlorine atoms as occupying seven of the corners of a cube, we can form two complete cubes by bringing two chlorine

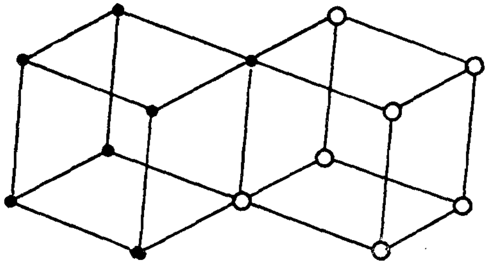

FIG. 23.—Structural formula of chlorine molecule.

atoms together edge to edge, as shown in Fig. 23. For the sake of clearness the electrons belonging to one atom are represented as circles, those belonging to the other as dots.

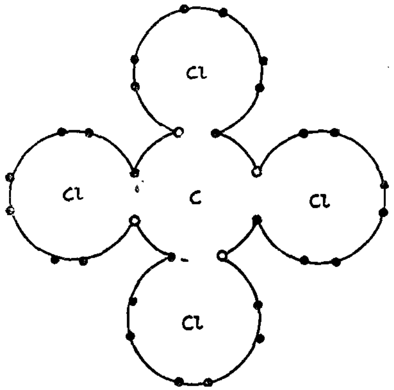

FIG. 24.—Structural formula of $C.Cl_4$.

Pairs of electrons which function simultaneously in two atoms are called duplets. Since no electron has been transferred from either atom to the other each atom remains neutral as a whole.

The extension of this idea to cover the case of the exercise of negative valencies in the case of other non-ionised molecules is quite simple. Taking the case of carbon tetrachloride, for example, where, as we have already stated, we have clear evidence that there is no molecular ionisation, it is only necessary to assume that one electron from each chlorine atom functions with one of the four carbon electrons to form a duplet. The structure of the molecule will then be that indicated in Fig. 24. To avoid confusion the electrons in this figure are all represented as being in the same plane. Fig. 23 could have been represented in the same way, and until

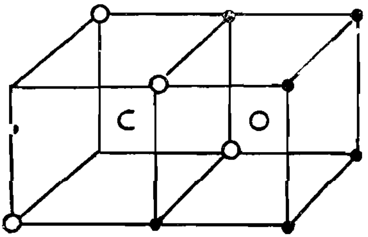

FIG. 25.—Structural formula of carbon monoxide.

we have more direct evidence on the point it is not very material which of the two methods we adopt. This duplet linking, is, of course, confined to compounds in which there is no molecular ionisation.

The existence of unsaturated compounds presents no real difficulty to the electron theory. Let us take, for example, the case of carbon monoxide, where the molecule is known to be non-ionised. Here the oxygen atom is saturated, but the carbon atom is not. On Sir J. J. Thomson's theory we may represent the molecule by the formula $\mathrm{C}\overset{\rightarrow}{\underset{\leftarrow}{\leftrightarrows}}\mathrm{O}$. On Langmuir's theory the arrangement might be represented by two cubes as shown in Fig. 25. It will be seen that there are still two unbound electrons in the carbon atom, but it will also be seen that

the mobility of these electrons is much impaired by the fact that the remaining two are now firmly bound to the oxygen group. They have less space in which to move, and the ease with which they can adjust themselves to attract some other atom is distinctly lessened. The question as to whether the decrease will be sufficient to allow the compound to exist in a free state or not will depend on the nature of the atom with which the carbon is combined. In the case of carbon monoxide the loss of mobility is sufficient to make the compound comparatively stable. In the corresponding case of CH_2 (which does not exist under normal conditions, although it has been identified in the positive ray tube) the effect of the two hydrogen atoms is insufficient to prevent the union of two neighbouring systems to form C_2H_4.

It is outside our purpose to pursue the theory of valency into its minuter details. In fact we have already gone as far, or perhaps somewhat further, than we are justified by our present physical knowledge of the structure of the atom. It must suffice to say that, by means of additional hypotheses, which, however probable they may be from chemical considerations, have not yet come within the scope of physics, Langmuir has succeeded in collating a considerable number of chemical facts in a very satisfactory manner. For these the reader may be referred to the numerous papers by Langmuir, in the journal of the American Chemical Society, from 1919 onwards.

A very hopeful suggestion, which has the advantage of including the suggestions both of Thomson and Langmuir is that in unionised compounds, one or more electrons, the " duplets " of Langmuir's theory, enlarge their orbits so that they surround both the atomic nuclei in the molecule, and thus might be legitimately regarded as belonging to both atoms. The spectra of these compounds should provide us with a means of solving the problem. Unfortunately they are invariably very complicated, and are only beginning to yield to analysis. It is on these lines, however, that we may hope for further progress.

CHAPTER VIII

THE ATOM IN VIBRATION

It can easily be shown that when a moving electric charge is accelerated or retarded in any way, a wave of electro-magnetic disturbance radiates out through the surrounding space. Consider an electron with its Faraday tubes moving along in the direction AB (Fig. 26). If the electron is moving with uniform velocity these tubes will

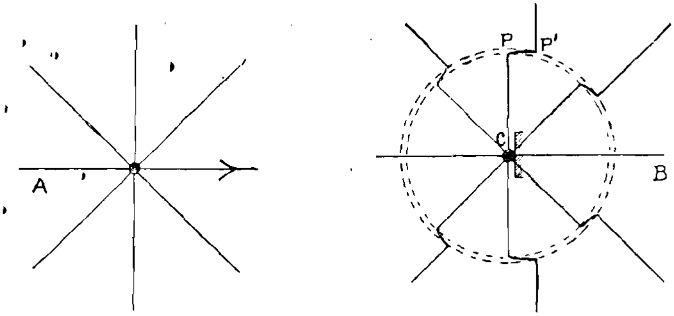

Fig. 26.—Production of electro-magnetic disturbances by the stoppage of an electron.

travel along with the electron as if they were rigidly attached to it. Suppose, however, that this electron on reaching a point C is suddenly stopped in its career. The ends of the Faraday tubes attached to the electron are suddenly brought to rest.

Now a Faraday tube is in some respects very like a stretched rope. For instance, it has a tension along its length, and possesses, as we have seen in a previous chapter, mass. Thus, just as when one end of a rope is jerked, a certain definite time elapses before the displace-

ment reaches the other end, so a displacement in a Faraday tube does not reach all points of it simultaneously, but is propagated along it with a definite velocity. In the case of the stretched rope the velocity is equal to $\sqrt{\frac{T}{m}}$, where T is the tension on the rope and m its mass per unit length. On similar principles it can be shown that the velocity of a disturbance along a Faraday tube is equal to $\frac{1}{\sqrt{\mu K}}$, where μ is the magnetic permeability and K the specific inductive capacity of the medium through which the disturbance is travelling. We will call this velocity V.

Now, during the time it has taken for the jerk to travel from the electron O to a point P, the portion of the tube beyond P, not having received the signal that the electron has been stopped, has been travelling on with its original velocity and is now in the position P′, where PP′ is the distance which the electron would have gone in the time taken for the disturbance to travel along the tube from O to P. Thus a kink is developed in the tube, which travels outwards along it with the velocity V.

The bent portion of the tube PP′ is moving perpendicular to its length and will thus, by the principles we have already developed, produce a magnetic field in the medium, which will also travel out with the kink. If we consider all the tubes surrounding the particle, it will be seen that these bent portions will form a kind of sheet of disturbance travelling outwards as an expanding spherical shell or wave.

If we can determine for any medium the values of μ and K in the same system of units, we can calculate the velocity V with which the disturbance is propagated in that medium. It will be remembered that the electrostatic system of units was obtained by defining K the specific inductive capacity of air as unity. The electromagnetic system, on the other hand, assigns this value to μ the magnetic permeability of air. The comparison of the two systems can best be performed by measuring the

capacity of the same condenser according to both systems of units. This operation is described in most text-books of electricity, and its details are outside the scope of our present work. The results obtained are, however, most striking and important. The result of a long series of experiments at the American Bureau of Standards, extending over several years, has given a value for V of $2{\cdot}997 \times 10^{10}$ cm. per second. This is, within the limits of experimental error, identical with the best determinations of the velocity of light, which have given a mean value of $2{\cdot}998 \times 10^{10}$ cm. per second. The agreement between the values obtained for the two velocities is too close to be accidental. It affords a convincing proof of the electro-magnetic nature of light.

In the case we have considered where the particle is suddenly brought to rest a single pulse is formed, the thickness of which is equal to the distance through which the disturbance can travel in the time taken to stop the particle. Such pulses are given out when cathode rays in a discharge tube impinge on a solid anticathode. They give rise to the well-known phenomena of Röntgen or X-rays.

If, instead of stopping the particle dead, we cause it to oscillate about a mean position, a series of undulations will be set up in the Faraday tubes attached to it, such, for example, as are seen when one end of a long rope is shaken regularly to and fro. Thus a series of electro-magnetic waves move out from the vibrating electron, their frequency being equal to the number of vibrations made by the particle per second. Their wave length is equal to the distance travelled by the disturbance during the time of one complete vibration. If this lies between ·0004 and ·0008 mm. these waves will produce on our eyes the impression of light. This, in its crudest form, is the Faraday-Maxwell electro-magnetic theory of light.

Not only may light originate in the vibration of electrons; all our experiments drive us to the conclusion that such vibration is the only way in which light can be

produced. Uncharged matter is apparently quite incapable of setting up any kind of disturbance in the æther. It is the electric charge which serves as the only link between the two.

We can, however, proceed further than this. Modern research has enabled us to identify with certainty the vibrating systems which emit the myriad lines in the spectra of the elements with the electrons, with the properties of which we are now growing familiar.

Michael Faraday, with almost uncanny prescience, seems to have felt that the relation between magnetism and light must be of the closest, and sought for it with unremitting diligence. It is one of the little ironies of life that the only effect which he did discover (the magnetic rotation of the plane of polarisation) was one of the very few phenomena which theory even now is hardly adequate to explain. The effect he sought for was not discovered until, more than thirty years later, his experiments were repeated with stronger magnetic fields and far more powerful methods of spectrum analysis by Zeeman.

He found that if a source of light was placed between the poles of a strong electro-magnet, and the light emitted was examined spectroscopically, a curious change took place in the appearance of the different lines in the spectrum, each being split up or decomposed into two components when the light was viewed along the lines of force in the magnetic field, or three when viewed at right angles to this direction.

Let us consider briefly the effect of applying a magnetic field to the charged particles emitting the vibrations as they oscillate about their mean positions. In general the path described by a particle will be somewhat complicated. We can, however, resolve its motion in the usual way into vibrations parallel to and at right angles to the lines of force in the magnetic field.

The vibrations performed along the lines of the field will be unaltered by the application of the field, since the latter produces no mechanical effect on a particle moving

in its own direction. It will be quite different with those vibrations which are executed in directions at right angles to this. It is shown in works on mechanics that any harmonic vibration can be regarded as the sum of two circular motions of properly chosen amplitude and phase. For example, the harmonic motion of a particle A vibrating along the straight line BC (Fig. 27) is exactly equivalent to the motions of two equal particles P and Q describing the circles shown in the diagram with equal velocities, but in opposite directions.

It will be sufficient, therefore, and will lead to no loss of generality, if we consider the charged particles as

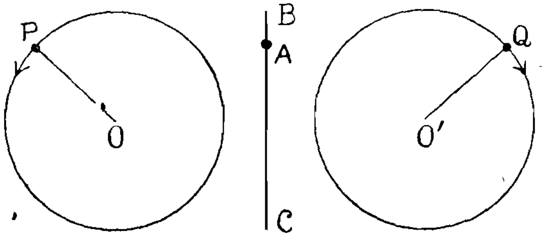

FIG. 27.—Illustrating the decomposition of a harmonic motion into two circular vibrations.

describing circles at right angles to the magnetic field, under the action of forces directed towards the centre of the circles. Since the motion of the charged particles is now everywhere at right angles to the magnetic field, there will be a mechanical force acting on the particles which will be everywhere at right angles to the magnetic field, and to the direction of motion of the particles. A little consideration will show that it must always act in the line joining the position of the particle at any moment to the centre of the circle.

Particles such as P and Q are, however, describing their circles in opposite directions. Thus the magnetic force will be in one case directed towards, in the other away from the centre of the circle. In the first case the total force

dragging the particle towards the centre is increased ; the circle is contracted and the time of vibration becomes more rapid. In the latter the effective force is diminished, with the result that the orbit expands and the vibrations become slower.

An apple whirling round at the end of a string will furnish a very useful analogy. If the tension of the string is increased the apple is drawn in, and its revolutions become *more* rapid. If, on the other hand, the tension is

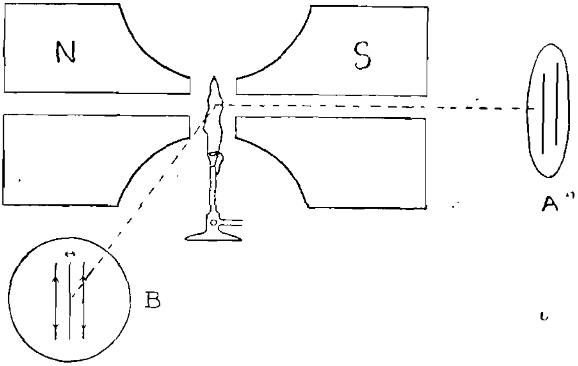

FIG. 28.—Illustrating the Zeeman effect. N, S are poles of electro-magnet. A, B represent the appearance of a single line emitted by the flame as seen through a spectroscope placed in the two positions.

relaxed, the apple takes a wider sweep, while the time it takes to complete a single revolution becomes longer.

Thus, instead of all the particles describing their orbits in exactly the same time, and thus producing light of one frequency only, one set have been accelerated, the other retarded by the magnetic field, so that instead of a single line the spectroscope will reveal two, one on each side of the original position of the line. By optical means we can distinguish between clockwise and counter clockwise rotations, and can thus determine which of the two has been accelerated and which retarded by the magnetic field. Since the effect on a positive particle would be

exactly the reverse of that on a negative, we can thus determine the sign of the charge carried by the vibrating particle. In every case so far examined it has been found to be negative.

If we view the flame along the lines of force, these two new lines are the only ones seen, as the vibrations taking place in the line of sight produce no effect on the eye. If, however, we look across the field, the vibrations executed along the lines of the field will also produce their effect in the spectroscope, and since their period is unaltered by the field they will give a line in the position of the original undecomposed line. Since all the circular paths are being now viewed end on, all three lines will appear to be plane polarised. These results are shown diagrammatically in *Fig.* 28.

This in its simplest form is exactly the effect discovered by Zeeman in 1896. He found that if a source emitting a line spectrum were placed between the poles of a very powerful electro-magnet and viewed with an interference spectrometer of high resolving power, the line was seen to be split up into three components when viewed at right angles to the magnetic field and into two when seen along the lines through a hole in the pole piece. This is very well shown in the photograph reproduced in Fig. 29. When, at the suggestion of Lorentz, who at once saw the correct explanation, the polarisation of the different components was examined, it was found to agree exactly with that described above.

We have seen that these observations have shown that the vibrating system is negatively charged. We can, however, go further than this. Following up the argument given above it can easily be shown * that if λ_a and λ_c are the wave lengths of the two outer components into which a single line of wave length λ_o is split up

$$e/m = \frac{\lambda_c - \lambda_a}{\mathrm{H} \cdot \lambda_o^2} \cdot 2\,\pi\,\mathrm{V}, \qquad (12)$$

* See Appendix C.

where e/m is the ratio of the charge to the mass for the particles, and V is the velocity of light. Now Runge and Paschen found that for a certain series of mercury lines, for example, the value of $\frac{\lambda_r - \lambda_n}{\lambda_n^2}$ was 2·14 for a magnetic field of 24,600 units, while V is, of course, 3×10^{10} cm. per

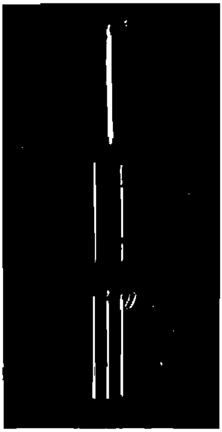

FIG. 29.—The Zeeman effect. (*a*) Undecomposed line. (*b*) Same line viewed along the lines of force of a magnetic field. (*c*) Line viewed at right angles to lines of force.

second. Substituting these values in the equation we have

$$e/m = \frac{2 \cdot 14 \times 2\pi \times 3 \times 10^{10}}{24,600} \text{ or } 1 \cdot 65 \times 10^7.$$

Considering that the displacement produced by even the strongest fields amounts generally to somewhere about one-fifth of the distance separating the two D lines of sodium, it will be seen that this result agrees even better than might have been expected with the value of the same ratio $1 \cdot 77 \times 10^7$ deduced for the negative electron from experiments on cathode rays. The identity of the light-

emitting systems with the cathode ray particles must be regarded as established beyond all challenge.

Since the lines in the spectrum of an atom represent different modes of vibration of the electrons connected with it, it should be possible, theoretically, to reconstruct the atom from a knowledge of its spectrum, just as it should, theoretically be possible to obtain some information as to the structure of a grand piano by listening to the noise which it makes in falling down a flight of stairs. The latter problem is much the simpler of the two. A contemplation of the spectrum of iron, with its many hundreds of sharp lines, wrung from the great American spectroscopist, Rowland, the exclamation that, compared with the iron atom, a grand piano is a very simple structure indeed.

Even so, spectroscopists had always felt that the problem was one which they ought to be able to solve, and some approach had been made towards a solution.

A careful analysis of the innumerable lines, which are dotted apparently at random through the spectra of the elements, has shown that they are by no means the confused jumble of periods which at first sight they appear to be. It was first pointed out by Balmer that the frequency ν of the principal lines of the hydrogen spectrum could be represented by substituting different integral values for τ in the equation

$$\nu = R\left(\frac{1}{2^2} - \frac{1}{\tau^2}\right) \quad . \quad . \quad (13)$$

the frequency being the number of vibrations made per second by the system emitting the light.

It was subsequently shown by Rydberg that Balmer's equation was only a particular case of a very general law. The more complicated spectra of the other elements can be sorted out into a small number of series, usually four for each element. All the lines in each of these series are capable of being represented by an equation very similar, though rather more complex, than that of Balmer.

The frequencies ν, of the different lines in any one series can all be obtained by putting n in the equation

$$\nu = \nu_0 - \frac{R}{(n + \mu)^2} \quad . \quad . \quad (14)$$

equal, in turn to any one of a succession of comparatively small whole numbers; ν_0 and μ being constants characteristic of the given series, and R a constant so universal that it applies to all the series of all the elements. It was further found that there was a connection between the values of ν_0 for the different series of the same element so that the whole of the lines in its spectrum could be represented by a general equation of the form

$$\nu = R\left(\frac{1}{(n' + \mu')^2} - \frac{1}{(n + \mu)^2}\right) \quad . \quad . \quad (15)$$

Here R is the universal constant, known as Rydberg's *constant, while μ' and μ depend upon the series and the* element; n' is a whole number and usually has the value 1, though occasionally it may be 2 or 3.

Relations of this type indicate a very close connection between the different lines in the spectra of the elements. The connection, however, is of a kind which is quite new to science, and one for which there is absolutely no analogy in the vibrations of any known mechanical structure. An organ pipe, for example, when sounded, gives out, in addition to its fundamental note, a whole series of overtones, to which, indeed, its fullness and richness are due. The frequencies of these overtones are always multiples of that of its fundamental, or, to adopt the language of the previous paragraph, they are given by substituting various whole numbers for n in the equation $\nu = n\,\nu_0$. A relation of this type, which is characteristic of mechanical vibrations in general, is clearly entirely distinct from that which holds in the realm of spectra. It seems evident that the laws which govern the emission of light from the atom must be very different in kind to those with which we are familiar in the world of mechanics.

There is a further difficulty, which may have already occurred to the reader. The spectra of the elements often contain an enormous number of lines, each of definite and distinct frequency. On the other hand the number of electrons in the atom is not very large.

The hydrogen atom, for example, contains only one electron. A single electron has only three degrees of freedom, and therefore only three modes of vibration, and in the simple atom even these three would all have the same period and thus coalesce into a single line. As a matter of fact, the ordinary spectrum of hydrogen contains a fair number of lines, while what is known as its secondary spectrum is very complicated. The difficulty seems at first sight almost insuperable.

To solve the riddle, Professor Sir J. J. Thomson has hazarded the bold, but almost certainly correct, conjecture that the lines in the spectrum of hydrogen and, indeed, of many other elements are not emitted by the atoms of the element at all, but by systems which only exist when the gas is thrown into a luminous condition. When we consider the absolute identity of the spectrum of an element whether situated on the earth or away on the furthest star of which we have spectroscopic data, this hypothesis may seem to be the most startling we have yet advanced. It is, however, not without a very considerable experimental basis.

Consider for a moment the phenomenon known as the selective absorption of light, of which the well-known experiment of the reversal of the sodium lines is a good example. If white light is passed through sodium vapour enclosed in an iron tube and the transmitted light examined with a spectroscope there can be seen across the ordinary coloured spectrum two sharp, dark lines, corresponding exactly in position with the two bright lines, which would be seen if the sodium were raised in incandescence. This is the cause of the dark Fraunhofer lines which are to be seen crossing the spectrum of the light from the sun.

These effects are due to a form of resonance. The

sodium atom contains systems of electrons which, when suitably excited, give out light of the frequency corresponding to the two sodium lines. To use an analogy from sound or from wireless telegraphy the sodium atom is tuned to this frequency. It will therefore begin to vibrate violently if oscillations of this period fall upon it. In doing so it abstracts the energy of the radiation in tune with itself, so that the latter is very rapidly absorbed, while light of frequency remote from this passes on almost unaffected. Thus, after passing through a very small

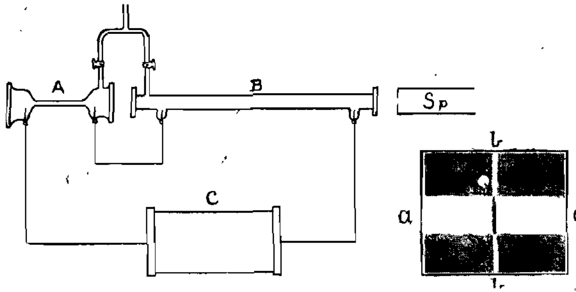

FIG. 30.—Ladenburg's experiment. A, discharge tube containing hydrogen at high pressure. B, discharge tube containing hydrogen at low pressure. C, induction coil working both tubes. *Sp*, spectrometer for viewing the light transmitted. The inset shows the appearance seen in spectrometer when the tubes are working. *a a*, broadened band due to hydrogen in A. *b b*, spectrum due to the tube B alone. The dark line where the two bands cross shows the reversal of the line by the systems formed in B by the discharge.

thickness of material, the light is robbed of all the constituents which have frequencies corresponding to those of the radiating systems within it. Hence all the systems which have natural periods falling within the limits of the visible spectrum must produce a dark band when white light is passed through them.

Now, it is remarkable that such absorption lines are not seen when white light is passed through a column of hydrogen, or indeed of most other simple gases. There are, for example, no dark lines to be seen in the spectrum

of light which has passed through a long tube of hydrogen gas, corresponding to, say, the brilliant lines of the hydrogen spectrum in the red or in the blue. Indeed, the laws of the absorption and dispersion of light in hydrogen are so simple that they can be explained on the assumption of a single absorption band far away beyond the violet end of the spectrum. This is, of course, what we should expect from the simple nature of the hydrogen atom. There is thus no escape from the conclusion that the vibrating systems which emit the hydrogen spectrum are not present in the gas in its normal condition.

A very interesting experiment due to Ladenburg has shown, however, that they can be manufactured in the gas under suitable conditions. He passed the light from a very bright discharge in hydrogen at fairly high pressure through a long tube of hydrogen at much lower pressure, fitted with terminals for the passage of a discharge, and examined the light transmitted with a spectroscope. His apparatus is indicated very diagrammatically in Fig. 30. The effect of the high pressure on the discharge is to widen out all the lines in the spectrum so that, instead of a narrow line, a broad band of light is seen overlapping the original line on each side. When there was no discharge passing through the long tube of hydrogen there was no trace of any absorption of any part of this broadened band.

If, however, a feeble discharge was sent through this long tube of gas it was seen that the centre portion of the broad line corresponding to the original line, and hence having the period of the light emitted by the tube at low pressure, became distinctly less bright than the outer portions, showing that the long column of feebly glowing gas was now absorbing from the light emitted by the brighter hydrogen tube those wave lengths corresponding in period to the light it was itself giving out. There are some difficulties in the experiment, and a certain synchronism of the two discharges seems to be necessary for its success. On the whole, the conclusion seems irre-

sistible. The hydrogen line spectrum is emitted by systems which are not present in the gas in its normal condition, but which are formed when the gas is thrown into a luminous state.

Let us consider for a moment the ways in which an atom can be made to emit luminous vibrations. Experiments have shown that for an atom to emit its characteristic spectrum it is necessary that it should be in a region of intense ionisation or recombination. It seems that nothing short of driving an electron into or out of the atom will suffice to set in vibration the light-emitting systems of electrons. It is obvious that this condition is fulfilled when the spectrum is excited electrically, either by sparking between terminals of the substance or by a low pressure discharge through a gas. It is interesting in this connection to note in the latter case that experiments have shown that, in the dark portions of the discharge the ionisation is very feeble while it is most intense in the brightest portions of the positive column. The ordinary method of producing a spectrum by placing the substance in a Bunsen flame is also merely a rough-and-ready way of producing ionisation in the substance. Professor H. A. Wilson having shown that a Bunsen flame, especially if it contains salt vapours, is the seat of very intense ionisation.

Let us suppose, to take the simplest possible case, that an electron is separated from an atom of hydrogen in any of these ways. Since each is temporarily free, neither will be capable of being set into vibration. We must, therefore, connect the actual emission of the spectral lines with the return of the electron to the atom, ionisation being merely a preliminary necessity for this return. The returning electron, attracted by the positively charged nucleus will approach it with an appreciable velocity. Ordinary mechanical considerations show that if the mutual kinetic energy of the two particles is of suitable magnitude the electron will begin to describe a closed path around the nucleus, in the same way that the earth

revolves round the sun and for precisely the same reasons. These revolutions will be isochronous like those of the earth, and will thus produce, according to orthodox electromagnetic theory, a single spectral line having a frequency equal to the number of revolutions made by the electron per second. It may be noted that this orbit may be entirely outside the normal atomic radius, and will not be occupied by an electron when the atom has returned to its normal state.

Here, however, we meet the difficulty which has confronted us before. If the law of force between the electron and the nucleus is that of the inverse square of the distance an orbit of any radius is mechanically possible under suitable conditions of energy. The greater the energy the wider the orbit. If we assume with classical electromagnetic theory that so long as an electron is describing a closed orbit it must be radiating, then the energy of the electron is being gradually dissipated and, hence, its orbit must be contracting. Each revolution will thus be a little quicker than the previous one, and the radiation emitted will thus form, not a single monochromatic line, but a continuous spectrum.

The difficulty could perhaps be met by assuming that the law of force between charges at distances comparable with the radius of the atom is not that of the inverse square. If, for example, the force between the electron and the nucleus had the form

$$\text{Force} = ee'\left[\frac{1}{r^2} - \frac{b}{r^3} + \frac{c}{r^4} - \frac{d}{r^5} + \ . \ \ . \ \ . \right]$$

then by taking r successively smaller and smaller it can be seen that the force would be alternatively positive and negative, that is—attractive and repulsive, and between each of these changes of sign there would be some critical distance at which the electron would be neither attracted nor repelled—it would be in equilibrium. Thus round each atomic nucleus there would be a series of shells on the surface of which an electron at rest would be in stable

equilibrium. This would produce exactly the arrangement of electrons in sheaths which we require for our atomic structure, without any necessity for assuming that the electrons were in rotation. At the same time for large distances between the charges all the terms except the first would be negligible, so that at ordinary distances the law would reduce that of the inverse square.

The suggestion, which is due to Sir J. J. Thomson, is a very attractive one, and would remove many of the difficulties which we have already experienced in building up an electronic theory of matter. Unfortunately, however, we can determine the law of force inside the atom by experiments on the scattering of α and β-particles by the atom. The experiments of Chadwick on the α-particles and of the author on the β-particles show that, at any rate up to a distance of 10^{-12} cm. of the centre of the atom, that is to say, practically up to the nucleus itself, the law of inverse squares holds with a considerable degree of accuracy.

We are thus thrown back again into the dark and mysterious hinterland where science is still in the making. There are, however, even here paths which seem hopeful. The subject is so important that we must defer it to a separate chapter.

CHAPTER IX

QUANTA AND ELECTRONS

Before taking our plunge into the unknown, it will be well to recapitulate the facts about which we have attained some certainty. We *know* that atoms consist of a massive nucleus of very small dimensions, in which practically all the mass of the atom is concentrated. We *know* that the charge on this nucleus is given by Ne where N is the atomic number of the element, and e the electronic charge. We are practically certain that the nucleus of the hydrogen, atom for which N is equal to unity consists of a pure electrical charge or proton, and that the nuclei of other elements are constructed of definite numbers of protons and nuclear electrons.

We *know* that the nucleus is surrounded by a number of electrons equal to the atomic number of the element, and that these electrons arrange themselves in a series of rings or sheaths around the central nucleus. We *know* also that the spectra of the elements are emitted by these electrons, and that the systems giving out these vibrations are not necessarily present in the atom in its normal condition. All these statements are as certain as any statement in Physics can be ; that is to say we could not deny any of them without recasting a very large part of our present physical conceptions.

On the other hand, the arrangement of a number of electrons around a nucleus which exerts a force inversely proportional to the distance is mechanically impossible if the electrons are at rest. It is possible, as we have seen, to overcome the difficulty by changing the law of force, but this suggestion is ruled out by direct and accurate

experiments. On the other hand, if the electrons are rotating in their orbits they should, according to the classical theory, be functioning as electromagnetic radiators, and would thus speedily be reduced to rest.

Stated in this way it seems clear that what is needed to bring harmony into the present discord is some new hypothesis as to the relation between radiation and the radiator. Is it possible that the classical theory is too wide, and that the acceleration of an electron does not necessarily result in the emission by it of radiation, and, if so, what conditions must be fulfilled in order that an electron may radiate? The question is one of fundamental importance, and it has been raised, not merely by our theoretical difficulties in atom building, but in a much more direct manner by certain well-authenticated experimental facts.

Let us take as a simple example the case of the relation between cathode rays and X-rays. We have already mentioned that X-rays are produced when a beam of cathode particles falls on a solid anticathode. The wave length of the X-rays emitted can be measured by means of the crystal diffraction grating. On analysing the resultant beam of X-rays, it is found to consist of rays of all frequencies up to a certain definite maximum value, which depends only on the potential applied to the discharge tube in which the cathode rays are produced. At this critical frequency the radiation absolutely ceases. If the potential is increased the maximum frequency is increased and conversely. In every case the spectrum is cut short at a definite point which depends only on the potential applied to the tube.

Now if V is the applied potential and e the charge on an electron, the maximum energy T of an electron in the cathode beam is Ve. If ν is the maximum frequency of the radiation emitted, it is found that ν is directly proportional to Ve to an accuracy which is certainly greater than one part in a thousand. Thus we can write—

$$T = Ve = h\nu \quad . \quad . \quad . \quad (15)$$

where h is a constant, which is quite independent of the construction of the tube. This equation is simply a representation of actual experimental observations.

Suppose that the X-radiation after travelling through a metre or so of air falls on a solid substance of any kind whatever. The X-rays are more or less absorbed, and, as we have already had occasion to mention, electrons are emitted by the absorbing substance. The velocity of these electrons can be measured by methods already described. It is found that no matter how far the X-rays may have travelled from their point of origin the maximum speed of these secondary electrons is almost exactly equal to the maximum speed of the cathode particles which produced the X-radiation. Thus the X-radiation is able to produce, at any distance, an electron possessing an amount of kinetic energy equal to that of the particle whose stoppage produced the ray. It is, in fact, found that the kinetic energy of the electron ejected is related to the frequency of the X-radiation producing it by exactly the same equation as that which relates the frequency of the X-radiation to the energy of the cathode particles producing it. Thus if T is the kinetic energy of the secondary electrons, and ν the frequency of the incident radiation, $T = h\nu$, where h has exactly the same value as before.

To understand how deeply these experimental results disturb our ordinary notions, we may take an illustrative example due to Sir Wm. Bragg. A sailor in New York harbour drops a heavy plank into the sea from a height of 30 ft. The fall of the plank sets up waves on the surface of the sea which travel out into the Atlantic. The energy of the plank like that of the electron impinging on a target, is converted into wave motion. Some of this will eventually reach the harbour at Liverpool. We should however be rather more than surprised if, at the moment of the arrival of this wave, a plank floating placidly on the surface of the dock should suddenly hurl itself upwards to a height of 29 or 30 ft. Yet this is

exactly what occurs when the X-radiation impinges again upon matter. It is clear that the relations between electrons and the waves they set up are very different from those ruling in ordinary mechanics.

These phenomena can be reproduced equally well in the luminous part of the spectrum. If, for example, we take a small vacuum tube containing sodium vapour at low pressure, and furnished with a Wehnelt cathode, and we apply a gradually increasing potential to the cathode, at first we see absolutely nothing. Suddenly, when the potential reaches a perfectly definite value the well-known yellow sodium spectrum flashes out. The sodium atom requires a definite amount of energy in the incident electron to yield its D lines, and this energy is related to the frequency of the D light by exactly the same formula which we have used for X-rays,

$$T = Ve = h\nu,$$

where h has exactly the same value as before. The value of V is known as the resonance potential for the ray emitted. In the case of the sodium D line it is about 2·1 volts. It is obvious that this constant h is a very important factor in the interchange of energy between an electron and electromagnetic radiation.

This conclusion had been arrived at, as early as 1900, by Planck from a study of the radiation from a heated body. In order to explain the observed distribution of energy in the spectrum of a hot body, Planck found it absolutely necessary to assume that the exchange of energy between matter and the æther took place not as a continuous emission or absorption of the radiant energy, but in certain perfectly definite, discontinuous, bundles or "*quanta*," as he called them. The energy T contained in one of these quanta of energy was directly proportional to the frequency of the radiation emitted or absorbed, and was given by the relation

$$T = h\nu,$$

where h is a constant, the value of which is exactly the

same as in the cases of the emission and absorption of X-rays and of sodium light already described. h is known as Planck's constant. Its value is $6{\cdot}555 \,.\, 10^{-27}$ (ergs) × (seconds).

We are thus compelled by a variety of phenomena to come, however reluctantly, to the conclusion that ordinary electromagnetic theory, as we understand it at present, does not represent in an adequate way the whole truth about the radiation of an electron. The electron does not go on radiating continuously until all its energy is gone. It gives out its energy in perfectly definite quanta, the magnitude of which is determined absolutely by the frequency of the radiation emitted. Conversely the electron cannot absorb continuously the radiation which may fall upon it. It must take in a whole number of quanta from the radiation. By no possibility can it either emit or absorb a fraction of this amount.

It is useless at present to speculate as to the mechanism by which this peculiar result is brought about. The merit of Planck's theory is not so much that it removes our troubles altogether, but that it packs them altogether into one bag, so to speak, so that they become easier to handle. For the rest we can only regard the matter as a child regards an automatic machine, content with the empirical knowledge that a penny inserted in the machine will permit the extraction of a bar of chocolate, and that two half-pennies, though commercially equivalent, will produce no chocolate whatsoever.

The fact that we can at present form no picture of the process of radiation makes the development of the subject extremely difficult. The nearest approach we can make to a picture is to consider an electron as a ball in a perfectly smooth cup. If we give the ball an initial velocity, it will roll round and round inside of the cup, with an amount of energy which, in the absence of friction, would remain perfectly constant. If the energy is increased, the ball will mount higher and higher up the sides of the cup until a definite critical amount of energy has been

imparted to it, which is just sufficient to carry it up to the rim. If a greater amount of energy is imparted it will fall out, giving up energy in the form of heat and sound as it crashes to the floor. Thus until the ball has been given a definite amount of energy it will conserve it all; if more than this is imparted to it, it will lose it.

It is highly improbable that this crude picture bears the slightest resemblance to the facts, but it may help us to an understanding of the consequences of the emission of energy by quanta. It is clear that on this hypothesis an atom will only emit radiation of frequency ν under very special conditions, one of which is obviously that it must have available an amount of energy at least equal to $h\nu$. If the radiating mechanism is not set in action (or to use our picture, if the electron is not projected over the edge of the cup) the electron may continue to describe its orbit for an indefinitely long time without any loss of its initial energy. In other words, the orbit will be stable, or, as Bohr prefers to call it, *stationary*.

The existence of non-radiating orbits is a necessary consequence of the theory of radiation by quanta. It is also clear that the electrons in the atom must arrange themselves in one or more of these stationary orbits, and will be in permanent equilibrium as long as they do so, though it by no means follows that there will be electrons occupying all the possible stationary orbits. In the normal state only a few such orbits, nearest the nucleus, will be occupied, since the electrons are attracted by the nucleus. An electron may, however, decribe one or more of the distant orbits when returning to the atom after ionisation has taken place. Radiation will not be emitted so long as an electron is in a stationary orbit. It will only take place when an electron passes from one orbit to another, or, in terms of our picture, when it falls from one cup into a lower one.

In this conception of stationary orbits to which the quantum ideas have brought us, we have clearly a solution of the unresolved difficulties of the previous chapters.

We see, certainly not *why*, but at least *how* the nuclear atom is to be made stable in spite of the fiats of classical electrodynamics; while at the same time we see some hope of answering (or evading) the enigmas raised in our last chapter.

The determination of the conditions which must be fulfilled that an orbit may be stationary was not easy, and several unsuccessful guesses were made before Bohr hit upon the correct solution. The law which he formulated is both simple and universal. Its main difficulty lies in the fact that it utilises a concept which had not previously found much place in science, and which, therefore, is not part of the ordinary equipment of the scientific mind. This is the idea of "action." We may arrive at this quantity most conveniently from a consideration of Planck's constant h.

Now h is a quantity of energy divided by a frequency, or since the frequency of a vibration is the inverse of the time of vibration, h is also the product of energy into time. This can also be expressed by saying that it is the product of momentum into distance. The amount of "action" set up by an electron, describing a circle of radius r, is equal to the momentum of the electron multiplied by the circumference of the circle, that is to say to $mv \times 2\pi r$. The facts which have given rise to the quantum theory can thus be expressed by saying that when energy is transferred from an electron to the æther, or from the æther to an electron, the amount of "action" transferred is always an exact integral multiple of the quantity h. Thus Planck's constant h may be regarded as the *atom of action*, just as the electron is the atom of electricity, and the quantum theory may be summed up in the statement that "Action is atomic."

It follows, therefore, that the action of an electron describing a stationary orbit must contain an exact number of these atoms of action, or expressed as an equation

$$mv \times 2\pi r = nh$$

where h is Planck's constant, and n is some whole number. This is the fundamental assumption made by Bohr in calculating his stationary orbits.

Now since an electron in a stationary orbit does not emit radiation it is clear that the ordinary laws of electrodynamics cannot logically be applied to it without radical alterations, of the nature of which we are profoundly ignorant. It can be shown, however, that the forces connected with the emission or non-emission of radiation will at any instant be very small compared with the ordinary electrostatic forces between the electron and the nuclear charge. We can, therefore, neglect them altogether without any appreciable error in calculating the equilibrium positions of the electrons, and assume that the ordinary laws of electrostatics and mechanics apply. Thus in Bohr's theory the orbits of the electrons are calculated *on the ordinary principles of mechanics and electrostatics*, and the quantum relation is then applied to pick out from the large number of mechanically possible orbits those few in which an electron can rotate without loss of energy, and in which alone, therefore, it is permanently stable.

The application of these principles to the simplest case of all, the hydrogen atom, presents no difficulties. According to ordinary mechanical principles, the electron will describe a circle around the nucleus. Mechanically, the radius of this circle depends only on the velocity with which the electron is moving, and a circle of any radius is possible, if the velocity is suitably adjusted. Applying the quantum condition it can be shown (see Appendix D) that the radii of the stationary orbits for the hydrogen atom are given by substituting whole numbers from one upwards for the symbol n in the equation

$$r = \frac{n^2h^2}{4\pi^2me^2} \quad . \quad . \quad . \quad (16)$$

where m and e are the electronic mass and charge. The radii of the successive stationary orbits are thus proportional to the squares of the natural numbers.

Now the total energy of an electron describing one of these orbits is partly kinetic, and partly potential, due to the fact that it is attracted to the central charge. If T_n is the total energy of an electron when describing the ring characterised by a number of quanta n it can be shown (see Appendix D) that

$$T_n = w_o - \frac{e^2}{2r_n}$$

where w_o is the potential energy of the electron when removed to an infinite distance from the nucleus. Suppose now that an electron passes from an orbit with n quanta to an orbit with only n' quanta. The energy given out will be equal to the difference between the energy of the electron in the two orbits, that is, to $T_n - T_n'$, or to

$$\frac{e^2}{2}\left(\frac{1}{r_n'} - \frac{1}{r_n}\right) = \frac{2\pi^2me^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n^2}\right)$$

on making the subtraction, and substituting for r_n' and r_n.

Now if this energy is given out in the form of radiation, the frequency of this radiation will by the quantum relation be obtained by dividing the energy liberated by Planck's constant h. Thus the frequency ν of the spectral line emitted will be given by

$$\nu = \frac{T_n - T_n'}{h} = \frac{2\pi^2me^4}{h^3}\left(\frac{1}{n_1^2} - \frac{1}{n^2}\right) \quad . \quad (17)$$

Thus the lines of the hydrogen spectrum should be given by substituting different integral numbers for n and n' in this equation.

Now this relation is obviously of the right form. If we put n_1 equal to 2 we at once get Balmer's equation (13), since all the factors outside the bracket are constant, and can be represented by a single constant quantity R. If we put n_1 equal to one we get $\nu = R\left(1 - \frac{1}{n^2}\right)$ which gives us the experiment relation between the frequencies of a series of hydrogen lines discovered by Lyman in the

ultra-violet part of the spectrum. If we make n_1 equal to three, we shall get a still further series of lines, which have been measured by Paschen, in the infra red part of the spectrum. All these relations are included in the general formula deduced by Bohr.

The diagram in Fig. 31 will perhaps help to make Bohr's theory of the emission of spectral lines clear to the

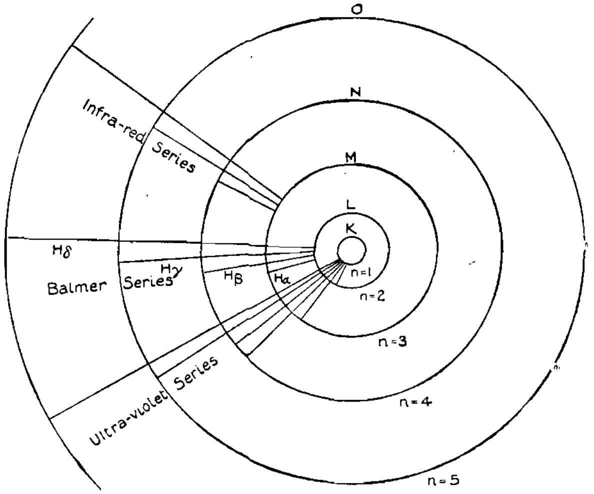

FIG. 31.—Illustrating Bohr's theory of the hydrogen spectrum.

reader. The successive circles represent different possible stationary orbits around the central hydrogen nucleus. The radii of these circles should increase as the square of the number, counting from the innermost one outwards, but for the sake of clearness it has been necessary to exaggerate the size of the inner rings. It is customary to letter these rings K, L, M, N, etc., the smallest one being the K ring. In the normal state the single hydrogen electron occupies the innermost or K ring. When, however, the atom is ionised, the electron is ejected from the system, and on its return it may, according to its

energy, begin to rotate in any one of these possible orbits, and when displaced from one of these orbits (probably by collision with other atoms, for all except the first of these orbits lie well outside the normal atom), it may fall into any one of the inner orbits, emitting in the process the radiation characteristic of this exchange.

Thus, Balmer's series is emitted by electrons which fall from outer rings into the second or L orbit. The H_α line is produced by an electron moving from the third orbit to the second, the H_β line by one which moves from the fourth to the second, and so on. Similarly, the ultra-violet series is due to electrons falling into the K ring, while the infra red series is due to electrons which fall only as far as the third or M ring.

We can, however, subject the theory to a much more searching test than this. If we examine the terms outside the bracket in equation (17) we shall find that we know from direct measurement the value of each one of them with an accuracy approaching one part in 1,000. The experimental value of the constant R can be determined from spectrpscopic observations with an accuracy of at least one part in 1,000,000. The measure of agreement between the value calculated from Bohr's theory and the value determined spectroscopically will provide such a test as only the best constructed theory could hope to survive. There are no uncertainties, no unknown factors, behind which it can take cover. The value of R determined from the hydrogen spectrum is $3{\cdot}2882 \times 10^{15}$. If in the expression $\frac{2\pi^2me^4}{h^3}$ we put $e = 4{\cdot}774 \times 10^{-10}$, $h = 6{\cdot}555 \times 10^{-27}$ and $e/m = 1{\cdot}765 \times 10^7$ which are the latest values for these quantities we obtain for Bohr's constant, $3{\cdot}2865 \times 10^{15}$. The agreement may well be said to be perfect.

This initial success of Bohr immediately gave a fresh impetus to theoretical and experimental research. It is doubtful if science has ever witnessed such an outburst of speculation and calculation. The foundations of the new

quantum mechanics are still far from settled, though progress has been made in many directions. The spectrum of any atom consisting only of a nucleus and a single electron can be determined by the method adopted by Bohr for the hydrogen spectrum. It is, in fact, as is shown in Appendix D sufficient to multiply the constant R by the square of the nuclear charge. Thus an atom having a nuclear charge 2 and a single electron would have a spectrum represented by

$$\nu = 4R\left\{\frac{1}{n_1^2} - \frac{1}{n_2^2}\right\}$$

Such atoms do not exist normally. They would, of course, be electrically charged. By subjecting helium to a very intense electrical discharge we can, however, strip it of both electrons, or, in other words, reduce it to an α particle. On the return of the first of these electrons the atomic system consists of a single nucleus and a single electron. The spectrum of this singly charged helium atom had already been discovered by Pickering and Fowler, and was found to fit in exactly with the formula given by Bohr. Recently Millikan has succeeded in stripping, in this way, all the electrons from the atoms of most of the elements up to fluorine, and the spectra of these stripped atoms agree exactly with the calculations of Bohr.

Difficulties commence as soon as we add a second electron to our atomic structure. We are then faced at once with the problem of the behaviour of three or more gravitating bodies, a problem with which mathematicians have wrestled in vain through the centuries. Even so simple a structure as the helium atom has so far defied exact analysis. It is clear then that, at present, we cannot deduce the atomic structures of the heavier atoms from first principles by purely abstract reasoning, though this, no doubt will come eventually. At present we must be satisfied to proceed by a judicious mixture of mathematics and empiricism, and be content to use

the experimental evidence which the spectra of the elements present to us so freely, now that we have the key to the language which they speak.

We have seen that Rydberg's formula (15) giving the frequencies of the lines in the line spectra of the elements in general is of the same form as that deduced by Bohr for the hydrogen atom. It differs from it only in the fact that we have to write $1/(n + \mu)^2$ instead of $1/n^2$ in each of the terms, as they are called, of the equation. The addition of the correcting factor μ probably implies that in the more complicated atoms the presence of the other electrons causes some modification of the simple inverse square law of force. Thus $\frac{R}{(n_1 + \mu_1)^2}$ represents, on Bohr's hypothesis, the energy of the electron in the orbit of arrival, and $\frac{R}{(n_2 + \mu_2)^2}$ its energy in the orbit from which it came. We can thus determine experimentally the energies associated with the orbits concerned in the production of spectral lines.

The optical spectrum of an element is, as we have already seen, due to the electrons in its outer shell. In fact, the transitions which give rise to the lines in the optical spectra mostly take place between orbits which are not normally occupied by an electron. The electron, being attracted by the nucleus will always fall ultimately into the lowest orbit which is open to it. In hydrogen, for example, it will occupy the first, or K orbit. The calculated radius of this orbit agrees, in fact, very closely with the estimates of the radius of the hydrogen atom deduced from the kinetic theory of gases. The higher orbits, in the case of hydrogen are only potential, that is to say the electron may circulate in them for a brief fraction of a second on its way back into the atom, but it will not stay there permanently. The electron falls back into the atom like a cricket ball rolling down a flight of stairs, emitting a characteristic burst of energy at each step.

As the number of electrons in the atom increases the orbits which, for hydrogen, are only potential gradually become filled up with electrons, so that orbits which are only potential for hydrogen become actual for elements of high atomic number. At the same time, owing to the fact that the attraction of the nucleus becomes bigger as the charge upon it grows, they will also shrink in size. Bohr, however, makes the assumption, which is almost certainly true, that they are otherwise unchanged, and that the general scheme of the atom is not affected either by the extra electrons or the increased nuclear charge. In this way then, it becomes possible to build up a definite structure for the atom.

Before describing this, however, it will be necessary to mention an extension of Bohr's simple theory, which is due to Sommerfeld. We have been assuming that the path of the electron around the nucleus is a circle. Mechanically, however, it might equally well be an ellipse. The planets, for example, actually describe elliptic orbits around the sun. In the absence of any quantum conditions, ellipses of any shape would be possible.

Now a particle describing an ellipse may be said to have two kinds of motion. In the first place it certainly revolves around its central sun, but it also increases and diminishes its distance from the central sun as it revolves around it. If we insist, with Sommerfeld, that each of these motions shall be quantised separately, we limit very severely the number of ellipses which are possible as stationary orbits for the electron. In fact, the innermost orbit of all, having only one quantum altogether, can only be a circle. The L orbit, however, has two "quanta" available. Both these may go in circular motion in which case our orbit will be a circle. But we may also assign one of these "quanta" to the backward and forward, or radial motion, in which case we shall have an elliptic orbit of definite eccentricity. If we assigned both the "quanta" to the radial motion

we should have a straight line vibration, which would bring the electron straight into the nucleus. This is clearly impossible physically. Hence the L orbits will be of two kinds, and similarly the M orbits will present three possibilities. These elliptic orbits can be calculated exactly for the hydrogen atom, and some of them are shown in Fig. 32.

If the mass of an electron were invariable its energy

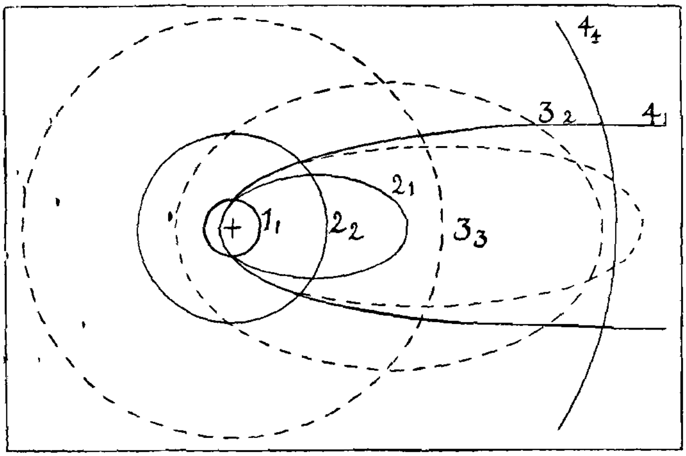

FIG. 32.—Some possible orbits of an electron revolving round a hydrogen nucleus.

would be the same whether it were describing a circle or an ellipse. Its mass, however, varies with its velocity as we have already seen, and Sommerfeld was able to show that owing to this variation, the energy of the electron describing an elliptic orbit will be a trifle less than when describing the corresponding circular orbit. It is usual to characterise the orbits by a large numeral giving the total number of quanta associated with the orbit, and a small subscript number giving the number of those quanta which are assigned to the circular motion.

Thus the circular L orbit is written 2_2 and the elliptic L orbit 2_1.

An appeal to the hydrogen spectrum triumphantly vindicated Sommerfeld's stringent demands. We have already seen that the hydrogen a line is emitted by an electron which falls from an M orbit into an L orbit, and its frequency is the difference between its energies in the two levels divided by Planck's constant. Now it

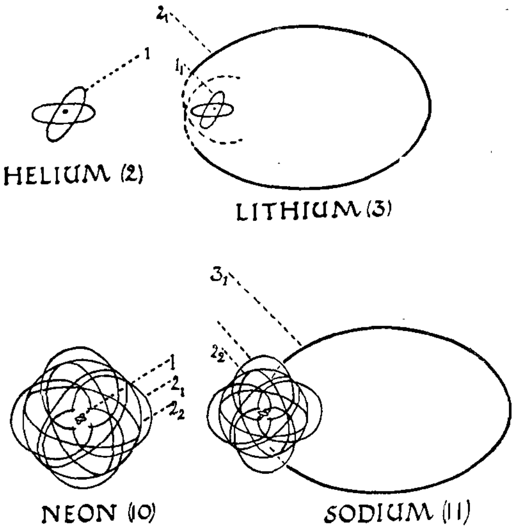

FIG. 33.—Some suggested atomic structures, after Bohr.

had long been known that this line is really complex, consisting of two separate lines quite close together, but differing perceptibly in frequency. The electrons giving out the separate components must have fallen through slightly different degrees of energy. The L level is, therefore, not one level but two, very close together, and on making the calculations the difference in energy between the circular and the elliptical L levels was found to be of exactly the right magnitude to account

for the observed difference in frequency between the two components of the hydrogen line.

It is impossible, here, even to indicate the elaborate processes by which Bohr, and others, have succeeded in building up the electron structure of the atom, and in assigning each of the electrons to its proper sphere of action. It is found that the two electrons in the helium atom each occupy a K orbit, or as we may catalogue it now a 1_1 orbit. It is still not known, with any exactness how these orbits are arranged with respect to each other, but it is generally assumed that their planes intersect at an angle of 60° as shown in Fig. 32. Elaborate calculations of the energy involved show that it is impossible to add another electron rotating at this distance from the nucleus. The K level is complete with two electrons describing their 1_1 orbits, and the next electron must remain satisfied with describing an L orbit, a 2_1 orbit since that is the one in which the energy of the electron is the least. Lithium, with three electrons will thus have the structure indicated in Fig. 33. The group of L orbits, which begin with lithium, are completed with neon, which thus consists of a kernel of two electrons with the helium structure, now very much reduced in size owing to the much greater force exerted upon it by the neon nucleus with its tenfold charge, surrounded by a group of eight electrons, two of which describe ellipses, while the remainder move in circles, with their planes inclined to each other at angles which cannot be determined with absolute certainty. It is difficult to represent so complicated a structure in a two-dimensional diagram, but Fig. 33 will perhaps convey some idea of what is meant. With sodium we commence the M orbits, so that the sodium structure exactly resembles that of lithium, except that the central swarm of electrons round which the single valency electron circulates has now the complex structure of neon, instead of the simpler one of helium.

The complete distribution of the electrons into their

TABLE IX.—THE DISTRIBUTION OF ELECTRONS AMONG THE DIFFERENT STATIONARY ORBITS IN THE ATOM

GROUPS		K	L		M			N				O					P	
ORBITS		1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2
1	H	1																
2	He	2																
3	Li	2	1															
4	Be	2	2															
5	B	2	2	1														
6	C	2	2	2														
7	N	2	2	3														
8	O	2	2	4														
9	F	2	2	5														
10	Ne	2	2	6														
11	Na	2	2	6	1													
18	A	2	2	6	2	6												
19	K	2	2	6	2	6		1										
20	Ca	2	2	6	2	6		2										
21	Sc	2	2	6	2	6	1	2										
22	Ti	2	2	6	2	6	2	2										
23	V	2	2	6	2	6	3	2										
24	Cr	2	2	6	2	6	5	1										
25	Mn	2	2	6	2	6	5	2										
26	Fe	2	2	6	2	6	6	2										
27	Co	2	2	6	2	6	7	2										
28	Ni	2	2	6	2	6	8	2										
29	Cu	2	2	6	2	6	10	1										
30	Zn	2	2	6	2	6	10	2										
36	Kr	2	2	6	2	6	10	2	6									
54	X	2	2	6	2	6	10	2	6	10		2	6					
86	Pr	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6

respective orbits has now been accomplished with fair certainty, and a selection of the results is printed in Table IX. It must be remembered that these arrangements have been arrived at almost entirely from spectro-

scopic data; it is a fascinating study to examine the table in conjunction with the periodic classification of the elements, and to see how much light it throws on some of the obscurer problems of this classification. If we admit that a theory is to be judged by the number and diversity of the facts which it correlates, Bohr's theory must be regarded as one of the most successful of modern times.

The lines on which the electron theory accounts for the first two short series of the periodic classification has already been dealt with at length in a previous chapter. We may, therefore, proceed immediately to a consideration of the peculiarities of the first long series of elements ranging from argon to krypton, including, that is to say, the elements having atomic numbers between 18 and 36. Now it will be seen from the table that the argon structure differs in kind from that of its predecessors in the inert gas family. In helium all the possible K orbits, and in neon all the possible L orbits are filled with electrons. In argon only the elliptic orbits of the M group are filled, the circular orbits are, as yet, untouched. The evidence for this is supplied by spectroscopy. The reason may, perhaps, be made clear from the diagram of the orbits given in Fig. 32. The elliptic orbits of the M group carry the electrons much nearer the nucleus than the large circular orbit. They are thus more closely bound to it, so much so in fact that the system acquires a stability comparable with that of the complete groups of neon and helium. Precisely the same considerations apply to the very excentric elliptic orbits represented by 4_1 and belonging to the N group, so that when a further electron is added, with the element potassium, it actually passes into a 4_1 orbit in preference to one of the still vacant 3_3 orbits, so that potassium has a structure precisely analogous to that of sodium and lithium; and, similarly, calcium has a structure closely analogous to that of beryllium, or magnesium.

At this stage matters begin to change. It appears

that there are only two of these highly excentric orbits. The next electron is thus presented with the choice of passing either into one of the circular orbits of the M group, or into one of the less excentric elliptic orbits of group N. As a matter of fact it passes into a circular M orbit. As we have been adding electrons we have also been increasing the nuclear charge on the atom, so that the M circles have been drawing in closer to the nucleus. The force with which an electron in one of these orbits is bound to the nucleus is thus increased, and the remaining M orbits rapidly fill up. In fact, for chromium (24) the binding force becomes rather greater for a circular M orbit than for the elliptic N orbit, and one of the N electrons passes back into the M ring. With copper, the M group is at last complete, but there is very little difference between the forces binding the last electrons in the M group and that binding the single electron in the N group. It is not until the nuclear charge has increased to 30 with zinc, that the M group may be regarded as completely stabilised.

We see then that, from the point of view of electronic structure, the peculiarity of these elements of the long series is the existence of a number of different orbits in the outer part of the structure of almost equal firmness of binding. The maximum valency of these elements increases uniformly from 3 to 7 as we pass from scandium to manganese, these being the numbers by which the electrons in the atom are in excess of the stable argon grouping. These surplus electrons are, however, subdivided among two types of orbits of slightly different degrees of firmness of binding, and there are similarities in the groupings of these outer electrons such as are not met with in the elements of the short periods. We should expect that this variation in the tightness of binding would lead to a corresponding variety in the number of electrons which might be lost. Thus these elements should be characterised by very variable valencies. This is, in fact, their most conspicuous chemical characteristic.

From the similarity in their outer structure we should expect a certain resemblance between their physical characters, and here again we find that the elements from vanadium to copper are physically much nearer akin to each other than they are to the elements with which they are usually grouped. Manganese, for example, both in its physical and its chemical properties is more nearly allied to iron than to fluorine. This difference is clearly brought out in the table, for, whereas fluorine by taking in a single electron can assume the stable neon structure, an additional electron would clearly not bring the manganese structure any nearer to a stable grouping.

With copper the normal course begins again, and copper has a structure formally equivalent to that of the alkalis, with a single electron in a highly excentric orbit. The last electron added to the 3_3 group is, however, not yet much more firmly bound than the one in the 4_1 orbit, so that copper shares properties both with the alkalis, and with the iron group.

Space will not permit us to follow out this interesting argument in further detail. Readers who are versed in chemistry will find no difficulty in doing so for themselves. The second long series proceeds on lines quite similar to those already discussed. With xenon, however, we have the typical 2, 6, arrangement, which completes its structure placed so far from the centre of the atom that a whole series of possible orbits (the 4_4 orbits, fourteen in number) are left unoccupied between it and the centre. The filling up of orbits so deep within the atom could hardly be expected to make much difference, either to the physical or the chemical properties of an atom. In this way Bohr accounts, in a highly satisfactory manner, for the existence of that strange anomaly the group of rare earth metals; a series of trivalent elements of atomic numbers ranging from 57 to 71, so very nearly identical that the greatest skill is required to separate them, so obviously alike that even the most ardent seekers after rigidity in the periodic classification have

been unable to do anything with them save put them all in the same square of the table. This very happy solution of one of the most difficult problems in chemistry is not the least among Bohr's many achievements.

It may again be emphasised that this scheme which we have been discussing has been worked out entirely from spectroscopic data, the assumption being made that an orbit, when once occupied, will not be seriously affected by further additions to the electronic structure. We are, however, not without the means of testing the completed structure. If we return again to Bohr's calculation of the hydrogen spectrum we shall see that each orbit is in reality characterised by the energy which an electron has when circulating in it, or, more precisely, by the difference between the energy of the electron in the orbit and its energy when completely removed from the atom. Now for any given atom we can measure experimentally the work which must be done to drag an electron away from any given orbit within it, and we can thus measure directly the energy associated with this orbit. We can thus, as it were, sound the depths of the atom as a plummet sounds the depths of the sea.

Our most convenient plummet is a beam of X-rays. Suppose we irradiate the atom with homogeneous X radiation of frequency ν. Quantum theory informs us that its energy will be done up in bundles of $h\nu$ each, so that the atom must take a whole bundle or none at all. Let us assume that absorption takes place in the K level. The atom now finds itself with $h\nu$ units of energy on hand, and proceeds to dispose of it by ejecting an electron from the K ring. This electron has initially the whole quantum $h\nu$. It expends, however, an amount w_k in getting away from the atom where w_k is the work which must be done to lift an electron from the K ring to the surface. Thus its kinetic energy on escaping from the atom is given by

$$\tfrac{1}{2} m v^2 = h\nu - w_k.$$

This velocity v can be measured by methods we have already described, and thus w_k can be at once deduced. Since the radiation may be absorbed in any orbit in the atom, we shall get sets of electrons escaping from the irradiated material with a series of definite velocities, and thus, by a single experiment, we can map out completely the different orbits, or energy levels as they are often called in this connection, within the atoms of our material. This method was originated by de Broglie, and has proved a very powerful and accurate means of investigating, in a perfectly direct manner, the electronic structure of the atom.

We may say, at once, that the results so obtained confirm Bohr's general scheme in a thoroughly satisfactory manner. In fact, the only change which these new experiments indicate as required is a rather more rigid subdivision of the elliptic orbits. It is found that the sets of elliptic orbits (but not the circular ones), which Bohr expresses by the same symbol, say 2_1 or 3_2, are, in reality, each divisible into two groups characterised by slightly different amounts of energy. Thus, from an energy point of view there are two levels represented by the symbol 2_1, and two levels represented by the symbols 3_1 or 3_2. The reason for this is probably connected with the forces exerted on the electron by the other electrons in the atom. This would account for the fact that this duality of the elliptic orbits is not observable in the optical part of the spectrum, where the orbits are virtual, and, therefore, outside the atom.

The theory of the electronic structure of the atom appears now to rest on very firm foundations. Space forbids even the mention of the many branches of physical phenomena which receive their first real adequate explanation in terms of this classification. The advent of the quantum, and its adaptation by Bohr to atomic structures mark an era in the progress of science comparable to those which resulted from the electromagnetic theory of light and the discovery of the electron. It must be

confessed, however, that these new ideas raise almost as many difficulties as they solve. Of the truth of our new laws there can be no doubt, but of their inner significance we are completely ignorant. The scientist, unlike Alexander, will never need to sigh for new worlds to conquer. Ever, as we make a fresh stride forward, new horizons disclose themselves. That is what makes science so tantalising, and so interesting.

CHAPTER X

THE MOLECULAR THEORY OF MATTER

We have now surveyed very briefly what is known and surmised of the nature and properties of the atom and molecule. In the brief space of the present chapter let us indicate one or two of the many points of interest which arise when we come to consider the molecule, not as standing by itself, but as massed together in myriads to form a fragment of what we know as matter.

In solids, we must regard the molecules as fixed relatively to each other, and we have in an earlier chapter considered briefly the nature of the molecular forces, cohesion, adhesion and the like, which bring about this result. But though the molecules are fixed, in the sense that they are not free to move about in the solid, we cannot consider them as being altogether motionless. Every body, unless it is at the absolute zero of temperature (a temperature which has not yet been reached in any experiment, although the brilliant researches of Kamerlingh Onnes have brought us within 2° of it), contains a certain definite amount of heat. Now heat is merely energy in a molecular form. The work which we do in raising the temperature of a substance is in reality spent in increasing the energy of the individual molecules of the substance, and thus in every body which is not at the absolute zero, the molecules must be in some sort of motion, the rapidity of which increases as the temperature is raised.

The molecules of the solid are not free to move from their positions, but two forms of motion are possible to them. They may either spin round like a top, or oscillate backwards and forwards about their mean position, like

the bob of a pendulum, or like a heavy weight suspended by an elastic cord.

In the case where the molecule is a system made up of two or more atoms, both these kinds of motion take place. The atoms spin round their common centre at a rate which increases as the body gets hotter, while at the same time the molecule as a whole oscillates backwards and forwards about its mean position with ever-increasing amplitude. If, however, the molecule consists of a single atom, only the latter form of motion seems to be possible, all the evidence going to show that thermal energy is unable to set a single atom spinning about its own centre.

For the sake of simplicity we will consider the case of the mon-atomic molecule, where the thermal energy is all used in the second kind of motion. As the body gets hotter and hotter, the molecule moves faster and faster, and the swings which it takes on each side of its normal position get larger and larger. The molecular forces which keep it in position, however, fall off very rapidly as the distance between the neighbouring molecules is increased, while at the same time the force required to retain the molecule in position increases with every increase in velocity. Hence, sooner or later, a point is reached when the molecular forces are no longer able to retain the atoms in position. The solid loses its cohesion and its rigidity. In other words it melts.

It is obvious that melting sets in when the temperature is just sufficient to give the molecules the necessary minimum of velocity to overcome the molecular forces retaining them in position—that is to say, it will be a constant for any definite substance. Also as work must be done to break down these inter-molecular bonds, it is evident that energy must be supplied to the body in the form of heat to enable it to melt. This is the latent heat of liquefaction.

Though the molecule has broken its old bonds, it is still within the range of molecular attraction of many of its neighbours, and has hardly escaped from one cluster before

it is attracted into another. Its rate of progress is thus comparatively slow. In time, however, any given group of molecules will be found dispersed throughout the whole of the liquid, and thus diffusion is brought about.

Consider now the state of affairs at the surface of the liquid. Every molecule, as we know, attracts every other molecule which may happen to be within a certain distance from it which we denote as the sphere of molecular attraction. In the body of the liquid, this attractive force is more or less neutralised by the fact that the molecule we are considering is surrounded on all sides by others, all pulling in different directions. Hence the combined effect is practically zero. At the surface, however, all the molecules are below it, and there are none above to neutralise the force which they exert. There is thus a strong downward force tending to drag the molecule into the surface. This force makes itself manifest in the phenomenon known as surface tension or capillarity.

A molecule will thus require a definite and in most cases a considerable velocity to succeed in escaping from the surface of the liquid. Now the mean velocity of the molecules depends only on the temperature, and is fixed for any given substance when the temperature is known. The actual velocity of any given molecule at a given instant may, however, differ very considerably from this average speed. The molecules in the liquid are constantly bumping against each other, and at every collision one of the molecules will probably gain speed, and the other lose it, and a difference in velocity is thus set up. The law of the distribution of speeds among an infinite number of colliding molecules has been worked out by Maxwell, for the simpler case of gas, and is known as Maxwell's law. He showed that at any given instant the great majority of the molecules would have velocities not widely removed from the average, but that there would always be a few which, owing to special circumstances, would have velocities very much greater, and others with velocities very much less, than the normal value.

Thus for oxygen at 0° C., in which the mean velocity of the molecules is 425 metres per second, out of every 1,000 molecules of the gas, about half have velocities between 300 and 500 metres per second, but there are 77 with a velocity greater than 700 metres per second, and thirty with a velocity greater than 900 metres per second.

The case of a liquid is much more complicated than that of a gas, but there is no doubt that a similar state of affairs prevails in the liquid state also. Hence, even at temperature far below the boiling-point of the liquid, there will be a few molecules which have temporarily sufficient speed to escape from the attraction of the mass of liquid below them.

Thus, even at low temperatures, a certain number of molecules escape every second from the free surface of the liquid. If the space above the liquid is free there will thus be a constant evaporation going on until all the liquid disappears in vapour.

If, however, the liquid is contained in a closed vessel, the escaping molecules are unable to get away altogether, and after perhaps many reflections at the enclosing walls will sooner or later strike the surface of the liquid and be re-absorbed. The number so returned to the liquid will depend on the number of molecules present in the vaporous state above the liquid. Evaporation will go on until the number of molecules in unit volume of the vapour is so great that the number returned per second is exactly equal to the number which escape per second owing to their high velocity. Thus for every temperature there will be a corresponding vapour pressure which will be constant for that temperature and that pressure. If the temperature is raised, the average speed of the molecules is increased, and more of them will attain a velocity sufficient to enable them to escape from the surface. The vapour pressure thus rises. When the vapour pressure reaches that of the atmosphere the liquid will begin to boil, and if the supply of heat is maintained, will all pass into the state of a gas.

The difference between a liquid and a gas is that in the latter all the molecules are moving with sufficient speed to escape completely from the attraction of their neighbours, and are thus able to avoid those molecular aggregations which take place in the liquid state. On this account the behaviour of a molecule in a gas lends itself much more readily to mathematical analysis than the more complicated phenomena of the liquid and solid states. The kinetic theory of gases has been very completely worked out by Maxwell, Clausius, and their successors. Unfortunately the theory needs considerable mathematical ability for its elucidation, and does not lend itself at all readily to non-mathematical treatment.

The pressure which a gas exerts on its boundaries is made up of the innumerable shocks given to the boundary walls by the many impacts upon them of the molecules of the gas, which are moving as we have seen with considerable speeds. It will obviously depend on the number of molecules present per unit volume, and the speed with which they are moving. The higher the temperature, the faster the molecules move, and the greater, therefore, will be the pressure they exert. It can be shown that this pressure is simply proportional to the temperature, if we begin to measure the latter not from the freezing-point of water, but from the absolute zero of temperature; that is, the temperature at which the molecules would all be reduced to rest. This temperature is about 273° below the zero on the Centigrade scale.

Again, if we halve the volume occupied by the gas, we double the number of molecules present in every cubic centimetre, and hence double the pressure which they exert on the enclosing walls. The pressure is thus inversely proportional to the volume occupied by the gas and directly proportional to its absolute temperature; thus, if P is the pressure, V the volume, and T the temperature of a given mass of substance in the gaseous form, P. V/T is a constant. This is the well-known gas equation embodying the laws of Boyle and Charles.

These laws are obeyed approximately by all gases, but perfectly by none. We have assumed in deducing the formula that the molecules exert no attraction upon each other *in the gaseous state*. This is, of course, only approximately true. Hence the velocity with which the molecules strike the boundary is always a little smaller than the normal velocity at that temperature, owing to the attraction of the molecules behind it. This effect will obviously be greater if the molecules are closely packed together than if they occupy a large volume. It has been shown that to get the true pressure we must add to the observed pressure an amount equal to a/V^2, where a is constant for a given gas.

Again the actual space in which the molecules are free to move is less than the whole space of the vessel, owing to the fact that the molecules are not mere mathematical points, but have a definite volume of their own. Thus, if b is the whole volume occupied by all the molecules in a gas, the actual empty space in which they are free to move is not V the volume of the vessel, but V — b.

To be accurate, therefore, we should write our gas equation in the form—

$$\left(p + \frac{a}{V^2}\right)\left(V - b\right) = R.T.,$$

where R is a constant for the gas.

This equation was first given by Van der Waals, and is found to represent the behaviour of real gases with a considerable degree of accuracy. In fact, it is even capable of representing with some degree of success the transition state from liquid to gas. It has the further advantage, that it offers us a simple method for determining the one molecular dimension with which we are still unacquainted, namely, the radius of the molecule.

By accurate experiments on the behaviour of the gas under varying conditions, we can determine the value of the constant b in any given case. Since one molecule cannot pass between two others if the space between them

is less than the diameter of a molecule, the volume b occupied by the molecules in the gas will be somewhat greater than the sum of their individual volumes. If r is the radius of each molecule, and N the total number of molecules present in the gas, a number which we have already determined, it can be shown that—

$$b = \frac{5}{2}\left(\frac{4}{3}\cdot\pi r.^3\right) N,$$

assuming that the molecules are spheres. In compound gases, where there are several atoms in the molecule, this can hardly be the case; but in the case of mon-atomic gases where the atom is also the molecule, it seems a probable assumption. Hence knowing N, we can calculate the value of r, the radius of the molecule of the gas we are considering. A few of the values so obtained are given in Table X. It will be seen that they are of the order of 10^{-8} or one hundred millionth of a centimetre. The radius of an electron is 10^{-13} cms., or about one ten thousandth part of this. *The size of an electron thus* bears to the size of the molecule in which it moves very much the same relationship that the diameter of our earth bears to the diameter of its orbit round the sun. A

TABLE X.—THE RADIUS OF THE MOLECULE

Substance.	From Van der Waals' equation.	*From the viscosity.*	From the thermal conductivity.
Hydrogen	$1{\cdot}16 \times 10^{-8}$ cm.	$1{\cdot}23 \times 10^{-8}$ cm.	$1{\cdot}20 \times 10^{-8}$ cm.
Helium	1·15 ,,	1·09 ,,	—
Nitrogen	1·76 ,,	1·75 ,,	1·66 ,,
Oxygen	—	1·70 ,,	1·55 ,,
Argon	1·43 ,,	1·68 ,,	—
Carbon dioxide	1·70 ,,	2·09 ,,	2·16 ,,

molecule is therefore a system very similar in its relative dimensions to the solar system but on an infinitesimal scale.

The kinetic theory affords other methods of estimating the dimensions of a molecule, but their theory is too complicated to be attempted in the space that remains. The results obtained are included for the sake of comparison in Table X. The second column of figures gives the value of the radius deduced from considerations of the viscosity of the gas; the last column the value deduced from its thermal conductivity. The three values agree among themselves as well as could be expected.

Let us return now for a brief space to our solid again. Solids may be divided into two classes, according as they do or do not conduct electricity. It is also found that conductors of electricity are also good conductors of heat, while electrical insulators are generally very poor conductors of heat. We have by now come to connect electricity with electrons, and hence an electric current is a flow of electrons from a place of high to a place of low potential. We may regard a conductor, then, as a substance containing electrons which are free to move under the action of an electric field, while in non-conductors the electrons are fixed and unable to follow the impulse of the field.

How are these electrons set free? In the first place it may be noticed that the only good conductors of electricity are metallic; that is to say, electro-positive in character, substances which we know from other phenomena readily part with an electron under slight provocation. Now in a solid such provocation may well be supplied by the close propinquity of the neighbouring molecules. It is well known that a charged body will attract light uncharged substances. The attraction of a well-rubbed stick of sealing-wax for small pieces of paper is generally our first introduction to the science of electricity. The attraction is, of course, mutual, the force on the charged body being equal to that on the uncharged paper. Hence an electron in one atom is attracted by a neighbouring uncharged atom, and under favourable circumstances, and especially in the case of an atom only too ready to part

with its electrons, the attraction may well be sufficient to enable it to make its escape.

That some such assistance is necessary and is so given is shown by the fact that a metallic vapour is no better a conductor than any other gas at the same temperature. Thus, while liquid mercury at its boiling-point is an excellent conductor of electricity, the mercury vapour above it conducts little better than the air it displaces—that is, practically not at all.

The evolutions of electrons by the molecules of a metal are very similar to the evaporation of a liquid into a closed space—a phenomenon we have already described. It will go on until the number of electrons which are attracted by the positively charged residues and so recombine, is equal to the number of electrons which are given off by the neutral molecules in the same time. Thus for a given temperature there will be a definite pressure of electrons per unit volume in the metal, and we may, in fact, look upon the electrons as a kind of tenuous gas filling up the interspaces between the molecules of the solid. We must regard them as moving about in all directions in the solid with considerable velocities. The principles of thermo-dynamics would lead us to imagine that when equilibrium is established each of these electrons will have the same average energy as the molecules around it—that is to say, the energy corresponding to the temperature of the body at the time. This is an important point to which we shall return latter.

These electrons, if no electric force be acting, will be moving in all directions, so that if we take any cross-section of the metal the number of electrons crossing it in one direction will be the same as the number crossing in the opposite direction, and so the total transference of electricity across the section will be zero.

If, however, we apply an electric field to the body there will be a force on each electron urging it in the direction of the field. Thus, in addition to the irregular motion due to the heat energy of the body, there will be a steady

drift of electrons as a whole in the direction of the electric force.

Let us consider for the sake of simplicity a regular conductor such as a uniform wire. Let us apply an electric field X to the wire along its length. Then the force on every electron is equal to X*e*, where *e* is the charge on an electron, and it can be shown that the average velocity *v* of the electron due to the electric field is K . X*e*, where K is some constant which for the moment we will leave undetermined.

In one second all the electrons which are less than *v* cms. from a given cross-section of the conductor will be forced across it under the action of the field. The volume of this space is *v*A if A is the area of cross-section, and thus if there are N electrons per unit volume, each carrying a charge *e* the total charge passing through the given cross-section will be N*e* . *v*A units per second. But this is by definition the current along the conductor. Hence remembering that the velocity *v* is K . X*e* we have the current *i* is equal to Ke^2N . A . X.

If *d* is the length of the wire and E the difference of potential between its ends, the field X in the wire is equal to E/*d*. Hence finally

$$i = (K \, . \, e^2 N)\frac{A}{d} \, . \, E \quad . \quad . \quad . \qquad (18)$$

The current through a given conductor is thus directly proportional to the difference of potential between its ends, which is the well-known law of Ohm. We see that it is also proportional to the cross-section of the conductor, and inversely proportional to its length. We may thus write it—

$$i = \sigma \, . \, (A/d) \, . \, E,$$

where σ is written for the quantity in the bracket. This is a well-known expression for the current through a wire. The quantity σ, which is a constant for a given substance at a given temperature, is known as its specific electrical conductivity. Comparing the equations we see that the conductivity σ is equal to K . e^2N.

Now the constant K can be evaluated on certain probable assumptions and has been shown to be equal to $V\lambda/6RT$, where V is the velocity of the turbulent motion of the electrons, λ is the average distance traversed by the electron between one collision with a molecule and the next, R is the well-known constant from the gas equation, and T is the temperature of the conductor on the absolute scale. Hence, finally, the electrical conductivity of a substance is given by the expression

$$\frac{N e^2 \lambda V}{6 . R . T} \quad . \quad . \quad . \quad . \quad (19)$$

This relation contains several quantities which are at present unknown to us, and so we cannot put it directly to the test. Let us proceed, however, a little further.

Suppose now that instead of applying an electric field to the metal, we begin to heat one end of it. We have seen that the turbulent velocity of the electrons depends only on the temperature, and hence the electrons in contact with the heated area will begin to move with a greater speed than those in the colder parts of the substance. These electrons are moving in all directions, and so, in course of time, some will move away into the colder regions, carrying their increased velocity with them. Their places near the hot end will, of course, be taken by electrons from the colder parts, which in turn will have their motion accelerated by contact with the hot face.

Thus there will be a constant stream of quickly moving electrons from the hot end into the cold parts of the body, sharing their energy with, and thus increasing the velocity of the molecules there. But the temperature at any point in the body depends only on the speed with which the particles are moving. Thus to translate the process from molecular to molar physics, heat has been conducted from the hot to the cold parts of the body, and the rate at which this process takes place measures what is called the thermal conductivity of the substance.

Since then the free electrons play the principle *rôle* both

in the conduction of electricity and the conduction of heat, we should expect to find some sort of relation between the conductivity of a substance for heat and its conductivity for electricity.

It has long been known that good conductors of the one are also good conductors of the other, and, as long ago as the middle of last century, Wiedemann and Franz, by comparing the experimental results for a number of metals, discovered that the ratio of the thermal to the electrical conductivity had the same value for all metallic elements. Somewhat later Lorentz, by making the comparison at different temperatures, found that the magnitude of this ratio was simply proportional to the temperature at which the comparison was made, reckoned from the absolute zero of temperature. These results are well brought out in Table XI. The second column gives the

TABLE XI

Metal.	Ratio of thermal to electrical conductivity.	Temperature coefficient of the ratio.
Copper	$6{\cdot}71 \times 10^{10}$	·0039
Silver	$6{\cdot}86 \times 10^{10}$	·0037
Gold	$7{\cdot}09 \times 10^{10}$	·0037
Nickel	$6{\cdot}99 \times 10^{10}$	·0039
Zinc	$6{\cdot}72 \times 10^{10}$	·0038
Cadmium	$7{\cdot}06 \times 10^{10}$	·0037
Lead	$7{\cdot}15 \times 10^{10}$	·0040
Tin	$7{\cdot}35 \times 10^{10}$	·0034
Platinum	$7{\cdot}53 \times 10^{10}$	·0046

ratio of the thermal to the electrical conductivities at 18° C. for the metals given in the first column of the table. The last column gives the observed temperature coefficient of the ratio. If Lorentz's law is true, this coefficient should have the value ·00366.

For many years this empirical law of Wiedemann and Franz remained without explanation. The electron

theory of conduction would, however, as we have seen, lead us to expect with confidence some such relationship. We can, however, go further than this. We have already seen how to calculate the electrical conductivity of a metal. Its thermal conductivity can also be calculated if we assume that the heat is all carried by electrons. This assumption cannot be strictly true, because substances which are non-conductors of electricity still conduct heat to a small but finite degree. In this case the transference of heat is carried on by the molecules themselves, the heated molecules transferring their increased velocity to their immediate neighbours by the somewhat tedious process of repeatedly bumping against them. This method is necessarily slow compared to that of the freely moving electrons, and the very small thermal conductivities possessed by electrical insulators leads us confidently to suppose that the amount of heat transmitted in this way in a metallic conductor is very small compared with that carried by the electrons.

The free electrons in a metal behave, as we have seen, like a rarefied gas. We can therefore apply the results obtained for gases to them. The thermal conductivity of a gas has been worked out by Maxwell and others. The mathematical analysis of the problem would lead us too far. It is contained in all treatises on the dynamical theory of gases. It is found that the thermal conductivity of a gas is represented by

$$\tfrac{1}{2}N\,\lambda\,V\,R$$

where N, λ, V, and R have the same meaning as in th equation (19) for electrical conductivity.

Hence comparing the two equations we have—

$$\frac{\text{Thermal conductivity}}{\text{Electrical conductivity}} = \tfrac{1}{2}(N\,\lambda\,V\,R) \div \frac{Ne^2\lambda V}{6\,R\,.\,T}$$

$$= 3\,\frac{R^2}{e^2}\,.\,T.$$

This is a very simple relation indeed. All the quantities

with which we are unfamiliar have gone out, leaving only R the constant of the gas equation, *e* the ubiquitous electronic charge, and T the temperature on the absolute scale at which our comparison is made. Let us substitute for these symbols their numerical values, and so bring our theory to a critical numerical test. R in absolute units is equal to $1{\cdot}40 \times 10^{-16}$, while *e* in electromagnetic units is $1{\cdot}57 \times 10^{20}$. If the comparison is made at 18° C., as in Table XI., T is (18° + 273°) or 291° on the absolute scale.

Hence, the ratio of the two conductivities should be equal to—

$$3 \times \frac{(1{\cdot}40 \times 10^{-16})^2}{(1{\cdot}57 \times 10^{-20})^2} \times 291,$$

or

$$6{\cdot}95 \times 10^{10}.$$

The agreement with the experimental values given in Table XI. is satisfactory beyond the bounds of expectation. Since R and *e* are both independent of the temperature, it is evident from our equation that the ratio varies directly as the absolute temperature, as was discovered experimentally by Lorentz.

The electron theory of conduction has already achieved success in many directions. It has also met with not a few unsolved difficulties, which would need a treatise rather than a chapter to expound. Let us, therefore, leave the subject here, and take a final and farewell glance at our atom, this time in the throes of dissolution.

CHAPTER XI

THE ATOM IN DISSOLUTION

If the ideas which have been developed in the preceding chapters have any sort of foundation in fact, the title of the present chapter will hardly come as a shock to any reader. It may seem at first sight much more surprising that a system so complex as the one we have described and in such constant motion, when subjected to all the shocks, mechanical, chemical, and electrical, which an atom must undergo, should continue to exist in such a persistent and unchangeable way as is actually found to be the case.

The cause is probably to be found in the relatively enormous amount of energy associated with an atom, an amount which is quite out of proportion to the energy liberated by chemical reactions. It has been shown that the heat liberated by the transformation of one gram of radium into its final products is about 4×10^9 gram calories, or, roughly speaking, it is equal to the heat generated by the combustion of half a ton of coal. Compared with this enormous quantity the heat liberated in the most energetic of chemical reactions fades into insignificance. The formation of a gram of water, for example, is attended by the emission of about 4×10^3 gram calories. And yet this enormous quantity must only be a small fraction of the total energy in the radium atom. Radium, as we shall see, has an atomic weight of 226; the final product of its decomposition one of about 206. This atom, which is now known to be an isotope of lead, must possess a very large amount of energy of its own. The total energy in an atom must therefore be enormous, and

it is for this reason that efforts to transmute one element into another have generally failed.

The main outlines of the new science of radioactivity are perhaps familiar to all readers. The subject is one of profound interest, but it lies almost wholly outside the scope of such a work as this. We will, however, summarise

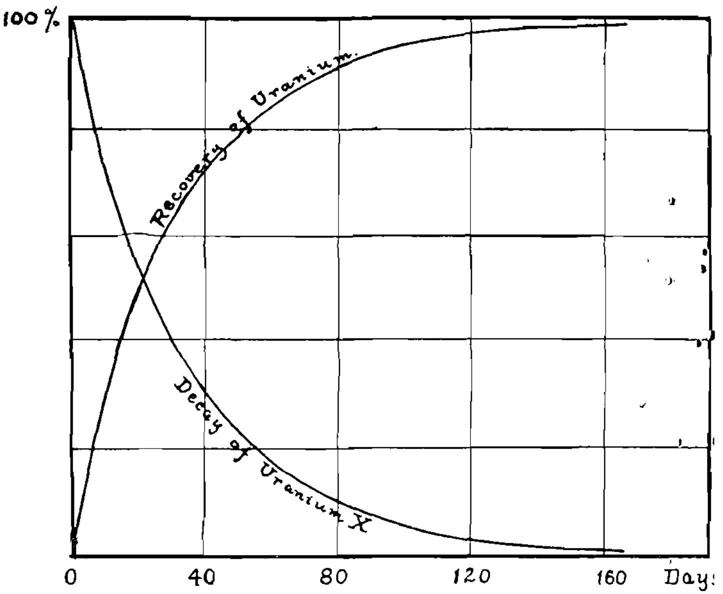

FIG. 34.—Growth and decay of β-ray activity with time for uranium and uranium X.

such of the main facts of that science as bear on our immediate subject, leaving the proof of the various statements and the description of the often very beautiful experiments from which they were deduced to other hands.

The metal uranium and its compounds were found by Becquerel to give off continuously particles capable of affecting a photographic plate at a considerable distance.

These are the β-rays which, as was mentioned in an earlier chapter, are identical except in speed with the cathode rays.

If the uranium salt is subjected to certain chemical processes it is possible to separate the uranium compound into two fractions. In one fraction, an almost imperceptible part of the whole, all the power of emitting β-rays is concentrated. The other, containing practically all the original salt, is completely inactive. For example, if we follow Sir William Crookes and shake up crystals of uranium nitrate in ether, the water of crystallisation, which settles out beneath the ethereal solution and can be separated from it by a separating funnel, is found to contain by far the greater part of the β-ray activity of the whole, the great mass of the salt now dissolved in the ether being comparatively inactive.

Let us take these two solutions and keep them under observation for some time. It will be noticed that the watery solution is gradually losing its β-ray producing powers, the rate of emission of these rays falling in fact to half its original value in about twenty-five days. At the same time the ethereal solution which we had rendered inactive gradually begins to radiate again, so that at the end of twenty-five days it has recovered one-half of its original activity. Fig. 34 shows in a graphic way the exact correlation between the loss of radioactivity by the active fraction and the growth of activity in the inactive mass. It will be seen that the total activity is constant throughout the experiment. From these results we may draw the following conclusions.

In the first place, the property of ejecting these electrons with enormous speeds resides not in the uranium itself, but in some substance which is mixed with it, and which can be separated from it by suitable chemical processes. Secondly, this substance is not a stable substance, but loses its activity with time. Lastly, this substance is not of the nature of an impurity in the uranium, but is so vitally bound up with it that when the latter is completely

freed from its presence it can reproduce this strange substance again at a steady and perfectly definite rate. The conclusion seems irresistible. Some new substance is being produced out of uranium itself, and in turn is decomposing with considerable celerity into some other substance which for the moment we are unable to trace.

I have discussed the case of uranium because that metal is a recognised element belonging to a well-known and respectable family, and might have been expected to behave in a rational and orthodox manner. The case of radium (which is actually a decomposition product of uranium) is still more striking. Rutherford discovered that radium and its salts are constantly giving off a heavy, chemically inert gas known as the "emanation," a non-committal name bestowed upon it before its nature had been determined. This emanation collects in the radium, but can be extracted from it by heating under reduced pressure, or, better still, by dissolving the salt in water and boiling the solution. In either way the radium can be completely freed from this new gas. On allowing the gas and the radium to stand, however, it is found that fresh emanation makes its appearance in the radium, while the collected emanation gradually disappears, the relation between the growth and decay of the emanation being precisely similar to that of uranium and its β-ray producing product. It is impossible to escape the conclusion that the element radium is evolving out of its own substance the heavy gas known as the emanation.

The properties of both radium and its emanation are now quite well known. Radium is a metal of the calcium group, with an atomic weight of 226·0. It has been prepared in a metallic state, and its properties are found to agree with the place we have assigned to it in the Periodic table. The emanation on the other hand is, as we have said, a chemically inert gas resembling the members of the helium group. It can be liquefied at $-65°$ C. Sir William Ramsay has even succeeded in determining its density, an achievement which as a triumph of skill and

refinement of experimental method is beyond all praise. The difficulties of the work will be realised when it is mentioned that the total volume of emanation available for the determination was less than one-tenth of a cubic millimetre.

The molecular weight of the emanation deduced from this determination is 222. Assuming the gas to be mon-atomic like the gases it most resembles, this is also its atomic weight.

What happens to that fragment of the radium atom which represents the difference between 226·0, the atomic weight of radium, and 222, that of its emanation? The answer is not far to seek. It will be remembered that radium is constantly giving off what are known as α-rays, which, as we saw in an earlier chapter, have been proved to be helium atoms with a high velocity and an electric charge. The atomic weight of helium is 4·0. Within the limits of experimental error this is the difference between the weight of an atom of radium and that of the emanation.

The break-up of the radium atom, therefore, takes place as follows: For some reason or other the nucleus of the radium atom becomes unstable, this instability resulting in the violent expulsion of a helium nucleus from the system. The huge velocity of the α-particles at first leads to the suggestion that the atom was in rapid rotation, and that the process resulting in the projection of the α-particle resembled the bursting of a fly-wheel. This is unnecessary. The mere electrical forces between charged particles so closely packed as those within an atomic nucleus would be quite sufficient to produce the velocities observed, as indeed we have seen in the case of the collision between the α-particle and the hydrogen atom. The ejection of the helium nucleus, and consequent decrease in atomic weight of four units enables the residual system to attain a temporary stability, the new element thus formed happening in this particular instance to be gaseous.

The emanation itself is very far from being stable. It is half decomposed in a little less than four days, the new decomposition product being in this case a solid. We

TABLE XII.

Atomic No.	Element.	Atomic Weight.	Half-value period.	Rays emitted.
92.	Uranium 1.	238·2	5×10^9 years.	α
90.	Uranium X_1.	(234·2)	24·6 days.	β (slow).
91.	Uranium X_2.	(234·2)	1·15 minutes.	β, γ
92.	Uranium 2.	(234·2)	2×10^6 years.	α
90.	Ionium.	(230·2)	200,000 years.	α
88.	Radium.	226	1,730 years.	α
86.	Emanation.	222	3·85 days.	α
84.	Radium A.	(218)	3 minutes.	α
82.	Radium B.	(214)	26·7 minutes.	β (slow).
83.	Radium C.	(214)	19·5 minutes.	β, α
81.	Radium C_2	(210)	1·4 minutes.	β
84.	Radium C_1.	(214)	10^{-6} seconds.	α
82.	Radium D.	(210)	16·5 years.	β (slow).
83.	Radium E.	(210)	5 days.	β (slow).
84.	Polonium.	(210)	136 days.	α
82.	Radio-Lead.	206·1	—	—

cannot follow here the changes undergone by the atom in its attempts to reach a stable state. They are, however, summarised in Table XII., which gives at a glance the whole of the interesting but pitiful story from the break-up

of the original uranium atom to that of polonium, the last radioactive member of the chain.

The decomposition product of polonium is not radioactive. The torn and distracted atom has found peace at last. It can thus no longer be investigated by those observations on the radiations emitted which have provided our principal means of following the long series of changes. Some uncertainty existed, therefore, for a time as to its nature. This has now been cleared up. It will be seen from the table that five α-particles are given out in the passage from radium to this final product of its decay. As each of these is a helium atom of atomic weight 4·0, the atomic weight of the final product should be 226·0 − (5 × 4) or 206. No element was known with exactly this atomic weight. Lead, 207·2, is the nearest, but unless our theory of radioactive change is wrong, the discrepancy between these numbers is greater than we can account for.

The matter has been finally settled by purely chemical means. Uranium minerals always contain a trace of lead. This lead has been extracted, and its atomic weight has been determined by the ordinary methods of chemical analysis. According to the latest measurements, the atomic weight of this lead is 206·1, a value extremely close to that which we have deduced from our radioactive data. There can be no doubt that this lead in radioactive minerals represents the last product of their radioactive decay, and that the product formed by the disintegration of polonium is this "radio-lead," which is thus an isotope of ordinary lead.

The chemistry of these radioactive substances, some of which have a life of only a fraction of a second, can be followed by considering the effect of the radioactive change on the resultant charge of the atomic nucleus. This resultant charge must be equal to the atomic number of the element. The expulsion of an α-particle lowers the atomic weight by four, and, since it carries a double charge, it lessens the resultant charge on the nucleus by two units.

In terms of the Periodic classification, it moves the atom two spaces to the left in the series. This is well illustrated in the case of radium itself, where the expulsion of an α-particle reduces radium, which, as we have seen, is obviously a member of the alkaline earth group, or Group II. of the table to radium emanation, which is equally obviously a member of the group of inert gases.

In some cases, however, the change is attended only by the expulsion of a β-particle. This will produce no sensible change in the atomic weight of the atom. Since, however, the β-particle carries a negative charge, its expulsion will increase the resultant positive charge on the nucleus by unity. Thus the expulsion of an α-particle by uranium (Group VI.) produces an element, uranium X_1, which must by our first rule be placed in Group IV. of the Periodic table. Uranium X_1 emits a β-particle to form uranium X_2, which by our second rule should be placed in one space to the right, that is, Group V. The emission by this substance of another β-particle moves the atom again one space to the right; that is to say, the product. Uranium 2 should occupy the same space in the table as the original uranium 1. The two uraniums should thus be isotopic. In fact the notion of isotopes was originated by Soddy from a study of the phenomena we are describing. Strong evidence in support of this theory is given by the fact that it has not been found possible by any chemical process to isolate uranium 2 from uranium 1.

The atomic numbers of the various elements in the uranium series are given in heavy type in Table XII. The atomic weights are given in ordinary type. Where the atomic weight is enclosed in brackets it has been deduced from our theory of disintegration. The numbers not so enclosed have been experimentally determined.

Occasionally the uranium 1 atom disintegrates in a different manner, giving rise to a second distinct radioactive chain, of which actinium is the principal member. This is not shown in the table. The element thorium is also radioactive, giving rise to another chain of products.

Altogether there are some thirty-five distinct radioactive elements to be fitted into the Periodic table between uranium and lead. The number of isotopes in some of the brackets is therefore considerable, but is not more than the number of isotopes to be found among non-radioactive elements, say, for example, krypton and xenon. The only distinction is that in the case of radioactive substances we are able to distinguish the different isotopes as different substances because their nuclei disintegrate in different ways, and have different degrees of stability. It is simply owing to differences in nuclear stability that we are able to divide the gas " emanation " into radium emanation, thorium emanation, and actinium emanation, while all the isotopes of the preceding member of the group are still called by the single name xenon.

So far we have been treading on safe ground. There can be no doubt that the scheme we have outlined so briefly above represents the true relation between the various radioactive substances. The disintegration theory, which is due to the genius of Sir Ernest Rutherford, as much of the work embodied in the table is due to his experimental skill and energy, is the only theory which can in any way explain this novel series of facts. It is now universally accepted. It is when we come to consider the mechanism of the change that difficulties arise.

Of actual knowledge we can hardly be said to have any, but something may be conjectured. In the first place it may be regarded as practically certain that the instability which leads to the dissolution of the atom arises within the nucleus of the atom. The nuclei of these heavy atoms are very complex structures. Since uranium has an atomic weight of 238, its nucleus must contain 238 protons, and as the atomic number is only 92, there must also be 146 electrons to reduce the resultant charge to this value. We have not even the shade of a hypothesis as to how these particles are packed away inside a space, the radius of which is certainly not much more than 10^{-12} cm.

The curve representing the decay of a radioactive

substance has been shown to be of the form known to mathematicians as exponential. Curves of this kind are generally connected with the law of probability. In the case of radioactive decay the curve may be interpreted as indicating that the chance of an atom of the substance disintegrating in a given short interval of time is simply proportional to the number of atoms of the substance present. It has been shown by experiment that an atom of emanation which has been in existence for three months is no more likely, and no less, to explode, than one which has just begun its existence. Disintegration has nothing to do with the age of the atom; it is just a matter of chance. The fact that no change in physical conditions has ever been found either to accelerate or delay the disintegration indicates that this chance is not that of some external accident; it is the chance that something will go wrong in the nucleus itself.

If we may hazard a guess—and it is nothing more—we may suggest that there may be several ways in which the particles in the nucleus may arrange themselves, and that occasionally the nucleus may pass from one of these groupings to another. One or more of these groupings may, however, in the case of the radioactive substances be unstable. The rate of decay would thus be a measure of the chance that the nuclear particles will fall into this particular grouping. This chance would not depend on the age of the atom, just as the chance of a penny coming down "heads" is independent of the number of times the penny has been tossed. The possibility that there may be more than one unstable arrangement would explain why uranium, for example, disintegrates in two entirely different ways.

It has been suggested that it is the nuclear electrons which are the disturbers of the atomic peace. It has been pointed out that whereas the expulsion of an α-particle seems to afford little relief to the atomic system, the expulsion of a β-particle is generally attended by a marked increase in stability in the resulting atom. An electron,

cut free from its moorings and able to pass from one configuration to another, would presumably radiate energy at each change, so that the nucleus would not be able to return again to its original form. Every fresh move on the part of the electron would result in a fresh loss of energy, and though a temporary stability might be achieved by the expulsion of α-particles, no final settlement could be arrived at until the loose electron was either safely moored once more, or expelled from the system. Whether there is any substance in the suggestion, perhaps time will show.

All the elements in the last series of the Periodic table are radioactive. The question naturally arises, Is this due to the structure of these heavy atoms having exceeded the limits of real atomic stability, or are we to regard all the elements, with the possible exception of helium, as liable to a similar but much slower decay? The problem is not urgent from a practical standpoint. Uranium requires something like five thousand million years to diminish to half, and the stability of the ordinary elements is certainly considerably greater than this. There is no immediate probability that the great globe itself will dissolve, "and like an insubstantial pageant faded, leave not a wrack behind" from any process of radioactive disintegration. The question is not without interest, however, on its theoretical side.

Extensive researches have been made to answer this question, but the results are perhaps not quite as definite as might be desired. Potassium has been found to give off appreciable quantities of β-radiation, its activity in this respect being about 1 per cent. of that of uranium. Its radioactivity, if such it is, seems to be of a peculiar kind, as in spite of very prolonged and drastic experiments, both by Campbell, who discovered the phenomenon, and by others, it has not been found possible to separate from the potassium any substance bearing the same relation to the potassium as uranium X bears to uranium. Rubidium and possibly cæsium show similar effects.

With all other elements the effect, if it exists, is very

small. There is, however, considerable evidence for the radioactivity of all kinds of matter, although it hardly amounts to a formal proof.

If we examine a quantity of air enclosed in a metal vessel we find that, even in the absence of any specific ionising agent, a certain number of ions are always being formed in the air, which enables us to send a small but measurable current through it. It has been shown that a great part of this ionisation is due to radium, which, disseminated through the atmosphere as emanation, or present in solid form in the soil, seems to be quite ubiquitous. It is found, however, that the amount of this ionisation depends on the substance of which the walls of the vessel are made: it is, for example, greater in a lead than in a copper vessel. This would certainly seem to point to the emission from the walls themselves of an ionising radiation of some sort, which is greater in amount for lead than for copper.

The matter is complicated by the fact that a certain amount of secondary radiation is set up when radium rays impinge on various metals, and these might very well depend for their intensity on the nature of the metal used. The feeble, but very penetrating radiation recently discovered by Millikan, and called by him the "cosmic" radiation, will presumably act in a similar way. Dr. N. R. Campbell, who has made this subject his own, decides against this explanation. I cannot do better than quote his deliberate conclusions:

"It has been proved beyond doubt that the emission of ionising radiation is an inherent property of all the metals investigated. It is not of course necessary that this ray emission should be identified at once with radioactivity—if that word is taken to mean a process of ray emission accompanied by atomic decomposition. But the constant intensity of the rays, and the probability that the larger portion of them are α-rays, afford considerable support for that hypothesis; while I know of no other process which affords any analogy."

The process is not proceeding at such a rate as to give cause for legitimate alarm. As we have seen, the average life of a uranium atom is about five thousand million years; from a comparison of the relative intensities of the radiation from uranium and from ordinary materials we may conclude that the average existence of the latter cannot be less than ten thousand times longer still. If, however, we accept Dr. Campbell's conclusion that all substances are emitting α-particles, then, whether quickly or slowly, all matter is in the process of gradual dissolution into helium.

It is curious that in this case the conclusions to be drawn from a sister science, that of Astronomical Physics, diametrically contradict those which we have arrived at from a consideration of radioactivity. It is a well-known fact that the very hottest and therefore, presumably, the newest stars, when examined by the spectroscope, are seen to consist of very little else than hydrogen, helium and two other substances, giving spectra which have not yet been identified on the earth. These are probably due to atoms in the making; perhaps a lithium atom which has not yet acquired its stable ring of electrons. Coming to some of the slightly cooler stars fresh elements, all of low atomic weight, gradually make their appearance, the list increasing, and elements of higher and higher atomic weight coming into existence as cooler and cooler stars are examined. As we have no reason whatever to suppose that the universe was anything save homogeneous in the beginning, we are led again to the conclusion that all the elements, as we have them on this earth, are in reality aggregates of hydrogen and helium.

In these stars progress is obviously from the simple to the complex. Little by little new elements are created by the gradual aggregation of the lighter atoms. On earth, so far as we can follow it, the change is in the opposite direction, the heavier atoms, such as uranium and thorium, spontaneously breaking down into simpler and simpler systems, a process which has also been brought

about artificially by Sir Ernest Rutherford for some of the lighter atoms. It must be remembered that so far as we know the decomposition of the radioactive elements is quite uninfluenced by any change of conditions which can be applied to them. The substance can be heated up in the electric furnace, or cooled to the temperature of liquid hydrogen, without in any way altering its slow but steady rate of decomposition. It is true that the highest temperatures which we can attain are small compared with those of the hotter stars, but it is difficult to conceive that a rise in temperature should assist aggregation, its tendency being always in the direction of disintegration.

The question suggests itself, Are the elements, as we know them, merely a part of a great cycle of growth and decay? Is the atom born to grow old, decay, and die? Are new atoms being formed in the secret places of the universe to take the place of those that have passed away? The facts have been briefly stated above, but of explanation there appears at present to be none. We are brought not for the first time to one of those mysteries which science has so far failed to illuminate.

We have weighed and measured the atom; we have analysed it and learned something of the stuff of which it is made and a little of its inner structure, and the way in which it behaves. We have watched its dissolution and attended its obsequies. Whether it will ever be granted to us to sit as spectators at a new birth time alone can show.

APPENDICES

APPENDIX A

(*See page* 42.)

DEFLECTION OF THE POSITIVE RAYS BY ELECTROSTATIC AMD MAGNETIC FIELDS

(1) *Electrostatic Deflection.*

Let d be the length of the path of the particles over which the field is applied, and D the distance of the photographic plate Z (Fig. 9) from the centre of the field MN. In the apparatus used d is small compared with D.

Since the field is uniform the particle is acted upon by a force X . E, and acquires an acceleration XE/m in a direction perpendicular to its initial velocity. This acts for the time t taken by the particle to describe the path d, that is for a time d/v. Hence velocity v' acquired under the action of the field—

$$= \frac{\mathrm{XE}}{m} \cdot t = \frac{\mathrm{XE}}{m} \cdot \frac{d}{v}.$$

The particle describes the remainder of its path from the field to the plate under these two velocities. Hence the deflection x is to the horizontal distance travelled D as the acquired velocity v' is to the initial velocity v of the particle. Thus—

$$\frac{x}{\mathrm{D}} = \frac{v'}{v} = \frac{\mathrm{XE}}{m}\frac{d}{v^2}$$

$$x = \mathrm{D} \cdot d \cdot \frac{\mathrm{XE}}{mv^2}.$$

(2) *Magnetic Deflection.*

The path of the rays in the field is bent into the arc of a circle of radius r where $r = \dfrac{mv}{\mathrm{H} \cdot \mathrm{E}}$.

On leaving the field the particles continue to move along the tangent to this circle at the point where the field ends. Hence the angular deflection θ of the beam is the angle between the tangents to this circle where the path enters and leaves the field respectively. This is obviously the same as the angle between the normals to the circle at those points.

Hence, if d is small compared with r, as is the case in practice, we have—

$$\tan\theta = \frac{d}{r} = d \cdot \frac{\mathrm{HE}}{mv}.$$

But, if y is the deflection as measured on the photographic plate—

$$\frac{y}{\mathrm{D}} = \tan\theta = d \cdot \frac{\mathrm{HE}}{mv}.$$

Hence—

$$y = \mathrm{D} \cdot d \cdot \frac{\mathrm{HE}}{mv}.$$

APPENDIX B

(See page 63.)

ELECTRO-MAGNETIC MASS OF AN ELECTRON

With the electron as centre describe two spheres of radius, r and $r + dr$, and draw two radii making angles θ and $\theta + d\theta$ with the direction of motion. If these radii are supposed rotated about the direction of motion of the electron, they will sweep out a hollow cone, cutting from the sphere of radius r a circular zone, the area of which is—

$$2\pi r \sin\theta \cdot r d\theta.$$

The volume of the space included between the two spheres and the hollow cone is thus—

$$2\pi r^2 \sin\theta \, d\theta \cdot dr.$$

The magnetic field due to the moving electron is obviously constant throughout the annular space so defined and equal to—

$$\frac{ev \sin\theta}{r^2}.$$

The energy of the magnetic field in the space is thus—

$$\frac{e^2v^2 \sin^2\theta}{8\pi r^4} \cdot 2\pi r^2 \sin\theta \, d\theta \cdot dr, \text{ or } \frac{e^2v^2 \sin^3\theta \, d\theta \cdot dr}{4r^2}.$$

Hence the total magnetic energy in the space between the two spheres is—

$$\int_0^\pi \frac{e^2v^2 \sin^3\theta}{4r^2} dr \cdot d\theta = \frac{e^2v^2 dr}{4r^2} \times 2\int_0^{\frac{\pi}{2}} \sin^3\theta \, d\theta.$$

$$= \frac{1}{3}\frac{e^2v^2}{r^2} dr \text{ . since} \int_0^{\frac{\pi}{2}} \sin^3\theta \, d\theta = \frac{2}{3}.$$

The total energy in the field is therefore the integral of this quantity from the surface of the electron of radius a to infinity.

I.e., total magnetic energy associated with the moving electron—

$$= \frac{1}{3} e^2 v^2 \int_a^\infty \frac{dr}{r^2}$$

$$= \frac{e^2 v^2}{3a}.$$

APPENDIX C

THE ZEEMAN EFFECT (CLASSICAL THEORY)

The mechanical force on the rotating electron P (Fig. 27, p. 127) is H . e . v, where H is the magnetic field supposed directed down through the paper, e the charge, and v the velocity of the particle. If P is positively charged, it will act towards the centre O, thus increasing the force retaining the particle; if negative, it will oppose it. The mechanical force on Q will obviously be in the opposite direction to that on P.

Let f be the retaining force in the absence of any magnetic field. Then, since the motion is simple harmonic, we may write—

$$f = k \cdot r,$$

where r is the radius of the circle described by the particle Also, by the laws of mechanics,

$$f = \frac{mv^2}{r} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If T is the time taken to complete the circle once

$$v = \frac{2\pi r}{T} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\therefore k \cdot r = \frac{m}{r} \cdot \left(\frac{4\pi^2 r^2}{T^2}\right), \; k = \frac{4\pi^2 m}{T^2} \quad . \quad . \quad . \quad (3)$$

Now, if T_1, r_1, v_1 are the values of T, r, and v for P when the field is applied, and T_2, r_2, v_2 the corresponding values for Q, we have—

$$\frac{mv_1^2}{r_1} = kr_1 + Hev_1 \text{ for P}$$

$$\frac{mv_2^2}{r_2} = kr_2 - Hev_2 \text{ for Q}$$

where the charge e is supposed to carry its own sign.

Substituting in these equations for the velocities v_1 and v_2

from (2), and for k from (3), and dividing the equations by r_1 and r_2 respectively, we have—

$$\frac{4\pi^2 m}{T_1^2} = \frac{4\pi^2 m}{T^2} + He \cdot \frac{2\pi}{T_1} \quad . \quad . \quad . \quad (4)$$

$$\frac{4\pi^2 m}{T_2^2} = \frac{4\pi^2 m}{T^2} - He \cdot \frac{2\pi}{T_2} \quad . \quad . \quad . \quad (5)$$

Subtracting (5) from (4)—

$$4\pi^2 m \left\{ \frac{1}{T_1^2} - \frac{1}{T_2^2} \right\} = 2\pi \cdot He \left\{ \frac{1}{T_1} + \frac{1}{T_2} \right\}$$

$$2\pi m \left\{ \frac{1}{T_1} - \frac{1}{T_2} \right\} = H \cdot e$$

$$\frac{e}{m} = \frac{2\pi}{H} \cdot \frac{T_2 - T_1}{T_1 T_2}.$$

or writing T_0^2 for $T_1 \cdot T_2$, which is permissible, since the change in the periods produced by the magnetic field is very small and T_0 lies between T_1 and T_2,

$$\frac{e}{m} = \frac{2\pi}{H} \frac{T_2 - T_1}{T_0^2}.$$

But if λ is the wave-length of the light emitted, and V is the velocity of light,

$$\lambda = VT.$$

Thus, if λ_0 is the original unaltered wave-length, λ_c that of the clockwise rotation, λ_a that of the counter-clockwise rotation,

$$\frac{e}{m} = \frac{2\pi}{H} \cdot \frac{\frac{\lambda_c}{V} - \frac{\lambda_a}{V}}{\frac{\lambda_0^2}{V^2}}$$

$$= \frac{2\pi}{H} \cdot \frac{\lambda_c - \lambda_a}{\lambda_0^2} \cdot V.$$

Thus, if the particles are positively charged, the clockwise rotation will have the greater wave-length ; if negative, counter-clockwise, as viewed along the lines of magnetic force. The latter is found experimentally to be the case.

APPENDIX D

THE HYDROGEN LINE SPECTRUM

Bohr's calculation of the frequency of the line spectrum of hydrogen can be put in the following simple form :—

Let e be the charge on an electron, m the mass of the electron, Ne the charge on the nucleus, v the velocity of the electron in its orbit which is assumed to be a circle of radius r.

Since the electron is describing a circle there will be a centrifugal force $\frac{mv^2}{r}$ acting upon it. For equilibrium this must equal the force of attraction between the electron and the nucleus. By Coulomb's Law this is equal to $\frac{e.Ne}{r^2}$. Hence our first condition of equilibrium is

$$\frac{mv^2}{r} = \frac{Ne^2}{r^2} \quad . \quad . \quad . \quad . \quad (1)$$

If t is the time taken by the electron to make one complete revolution in its orbit, the length of which is $2\pi r$, then its velocity v is given by

$$v = \frac{2\pi r}{t} \quad . \quad . \quad . \quad . \quad (2)$$

and on substituting this value in (1) we have

$$\frac{4\pi^2 mr}{t^2} = \frac{Ne^2}{r^2} \quad . \quad . \quad . \quad . \quad (3)$$

The kinetic energy of the electron $= \frac{1}{2} mv^2$

$= \frac{2\pi^2 r^2}{t^2} m$, substituting for v from (2)

$= \frac{Ne^2}{2r}$ by equation (3).

In addition, the electron has potential energy due to the electrostatic attraction of the nucleus. This is a maximum when the electron is as far away as possible from the nucleus. Let this maximum value be w_x. This is the work which must be done to remove the electron to an infinite distance from the nucleus. The work done in removing it to a distance r from the nucleus is $\frac{e.Ne}{r}$ by the ordinary laws of electrostatics. Hence its potential energy at a distance r from the nucleus is the difference between these quantities, and is equal to

$$w_x - \frac{Ne^2}{r}.$$

The total energy W_r of the electron in the orbit of radius r is thus given by

$$\begin{aligned} W_r &= \text{kinetic energy} + \text{potential energy} \\ &= \frac{Ne^2}{2r} + w_\infty - \frac{Ne^2}{r} \\ &= w_\infty - \frac{Ne^2}{2r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4) \end{aligned}$$

This result follows from ordinary mechanical principles. Applying now Bohr's condition for a stationary orbit we have (p. 145)

$$mv \,.\, 2\pi r = nh$$

$$\therefore \quad \frac{4\pi^2 r^2 m}{t} = nh \quad \text{from (2)}$$

$$\therefore \quad t = \frac{4\pi^2 r^2 m}{nh} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Substituting this value in (3) we get, after the usual algebraical simplification—

$$r = \frac{n^2 h^2}{4\pi^2 m N e^2} \quad . \quad . \quad . \quad (6)$$

This gives the radii of the stationary orbits, by substituting whole numbers for the factor n. Inserting the known values of h, m and e we have $r = \cdot 52 \times 10^{-8}\, n^2$ cm. The smallest ring has thus a radius of about $\cdot 52 \times 10^{-8}$ cm. Thus all the orbits except the first are *outside the atom.*

Substituting this expression for r in equation (4)—

$$\begin{aligned} W_r &= w_\infty - \frac{Ne^2}{2} \cdot \frac{4\pi^2 m N e^2}{n^2 h^2} \\ &= w_\infty - \frac{2\pi^2 m N^2 e^4}{n^2 h^2} \quad . \quad . \quad . \quad . \quad . \quad (7) \end{aligned}$$

The energy given out when an electron falls from an orbit of radius r_1 to one of radius r is therefore

$$\begin{aligned} W_{r_1} - W_r &= w_\infty - \frac{2\pi^2 m N^2 e^4}{h^2 n_1^2} - w_\infty + \frac{2\pi^2 m N^2 e^4}{h^2 n^2} \\ &= \frac{2\pi^2 m N^2 e^4}{h^2} \left\{ \frac{1}{n^2} - \frac{1}{n_1^2} \right\} \end{aligned}$$

If this energy is emitted as monochromatic radiation then by Planck's law the frequency ν of this radiation is given by $W_{r_1} - W_r = h\nu$, or

$$\begin{aligned} \nu &= \frac{Wr_1 - Wr}{h} \\ &= \frac{2\pi^2 m N^2 e^4}{h^3} \left\{ \frac{1}{n^2} - \frac{1}{n_1^2} \right\} \quad . \quad . \quad (8) \end{aligned}$$

For the hydrogen atom N = 1, since its nucleus carries a single charge. The lines of the spectrum of the hydrogen atom should thus be given by substituting different whole numbers for n and n_1 in the equation.

$$\nu = \frac{2\pi^2 me^4}{h^3}\left\{\frac{1}{n^2} - \frac{1}{n_1^2}\right\}$$

As will be seen from the analysis, n is the number of the ring into which the electron falls, n_1 that of the ring from which it starts.

The spectrum of a singly charged helium atom can be obtained by putting N = 2, since the helium nucleus has a double charge. If, however, there are electrons as well as a nucleus in the atom, the charges on the electrons must be taken into account in calculating both the orbit and the energy. The mechanism is that of three gravitating bodies, the solution of which has never yet been obtained.

TABLE OF ATOMIC DATA

(Calculated from the most recent observations.)

Mass of an electron m	$9{\cdot}0 \times 10^{-28}$ gm.
Charge on an electron e	$4{\cdot}774 \times 10^{-10}$ e.s. units. $1{\cdot}591 \times 10^{-20}$ e.m. units.
Ratio of charge to mass, e/m, for an electron	$1{\cdot}765 \times 10^{7}$ e.m. units per gm.
Radius of an electron	$1{\cdot}87 \times 10^{-13}$ cm.
Radius of positive nucleus of hydrogen atom (the proton)	10^{-16} cm.
Mass of hydrogen atom	$1{\cdot}66 \times 10^{-24}$ gm.
Radius of the K ring in hydrogen atom	$0{\cdot}53 \times 10^{-8}$ cm.
Radius of hydrogen molecule	$1{\cdot}21 \times 10^{-8}$ cm.
Radius of helium nucleus	4×10^{-13} cm.
Radius of platinum nucleus about	10^{-12} cm.
Number of gas molecules in 1 c.c. at 0° C. and 760 mm. pressure.	$2{\cdot}705 \times 10^{19}$
Planck's constant h	$6{\cdot}555 \times 10^{-27}$ erg. sec.
Velocity of light c	$2{\cdot}998 \times 10^{10}$ cm. per sec.

BIBLIOGRAPHY

THE following brief list may be of use to readers who wish to pursue further the subject treated in the foregoing pages. It lays no claim to completeness.

Professor Sir J. J. Thomson's *Conduction of Electricity through Gases*, and Professor Sir Ernest Rutherford's *Radio-active Substances and their Radiations*, formerly the standard works on the subject, are both now seriously out of date. Owing to the rapid growth of the subject it is doubtful whether a complete account of the phenomena can ever again appear in a single volume. Dr. N. R. Campbell's *Modern Electrical Theory* (3rd ed.) with its supplements now being issued is a fascinating and original treatise on electron theory as a whole. Excellent monographs on individual parts of the subject are available, of which Sir J. J. Thomson's *Rays of Positive Electricity*, Millikan's *Electron*, and Aston's *Isotopes* may be particularly commended. Sommerfeld's *Atombau und Spektrallinien* (Atomic Structure and Spectral Lines), of which there is now an English translation, is indispensable to the serious student of the subject, and Andrade's *Structure of the Atom* (3rd ed.) is a very valuable compendium of the subject.

These works are mostly of an advanced character, and demand some considerable mathematical equipment on the part of their readers. A fuller account of the subjects dealt with in this volume, which, however, makes less exacting demands on the reader than the advanced treatises referred to above, is provided in the present author's *Ions, Electrons, and Ionizing Radiations*. Perrin's *Les Atomes* (of which there is a good English translation), which treats the subject from a different standpoint, can also be strongly recommended.

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